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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Ethane and Propane. By L. MEYER (*Ber.*, 1894, **27**, 2767—2769; compare Abstr., 1893, i, 681).—The following physical constants of ethane and propane have been accurately determined.

Density of the liquid—

Temperature		0°.	+6·2°.	10·5°.	11·5°.	15·9°.
Density	ethane..	0·466	—	0·396	—	—
	propane	0·536	0·524	—	0·520	0·515

Vapour Pressure.

Temp.	Pressure in atmospheres.		Temp.	Pressure in atmospheres.	
	Ethane.	Propane.		Ethane.	Propane.
−89·5°	0·95	—	0°	23·3	—
−37	—	1·0	+1	—	5·1
−33	—	1·8	5·5	—	5·9
−31	11·0	—	12·5	—	7·1
−20	14·5	—	15	32·3	—
−19	—	2·7	22	—	9·0
−15	—	3·1	34·5	50·0	—
−11	18·3	3·6	53	—	17·0
− 5	—	4·1	85	—	35·0
− 2	—	4·8	102	—	48·5

Ethane boils at −89·5° at a pressure of 735 mm., and propane at −37° at a pressure of 760 mm.

Critical data—

	Ethane.	Propane.
The meniscus becomes indistinct at..	+32·0°	+101·0°
Gas and liquid are of equal density at	40·0	110·0
Formation of cloud on cooling commences at.....	34·5	102·0
At this temperature the pressure is..	50·0 atmos.	48·5 atmos.

A. H.

Preparation of the Paraffins. By L. MEYER (*Ber.*, 1894, **27**, 2766—2767; compare Abstr., 1893, i, 681).—The alcoholic iodides react with aluminium chloride in a different manner at different temperatures, as is shown by the following table of results.

Compound.	Temperature.	Product.
Normal propylic iodide.....	130°	Propane.
Isopropylic iodide.....	145	Propane.
Normal butylic iodide	140	Butane.
Secondary butylic iodide.....	80	Butane.
,, ...	160	Propane.
,, ...	225	Propane.
Tertiary butylic iodide	30	Butane.
,, ...	140	Propane and a little butane.
,, ...	150	Propane.
Isoamylic iodide.....	140	Butane.
Secondary normal hexylic iodide	80	Hexane.
Secondary normal hexylic iodide	90	Hexane and a little butane.
Secondary normal hexylic iodide	128	Butane and a little propane.
Secondary normal hexylic iodide	225	Propane.
Secondary octylic iodide	125	Butane.

By maintaining the correct temperatures, the products named can be obtained in a state of great purity. Propane undergoes no further change even at 225°. A. H.

Explosion of Acetylene with Oxygen. By L. MEYER (*Ber.*, 1894, **27**, 2764—2765).—The author records an instance of the explosion of acetylene with $2\frac{1}{2}$—3 vols. of oxygen in which the cylinder used was shattered, and even the foot, 2 cm. thick, broken into several pieces. In showing the explosion as a lecture experiment, precautions should, therefore, be taken to prevent the occurrence of accidents.

A. H.

Action of Chlorine on Trimethylene. By G. GUSTAVSON (*J. pr. Chem.*, 1894, [2], **50**, 380—383; compare Abstr., 1891, 159).—The

higher boiling portion of the product of the action of chlorine on trimethylene yields three compounds on further fractionation. These are trimethylenic chloride, $C_3H_6Cl_2$, boiling at 119—120°, β-chloropropylidene chloride, boiling at 146—148°, and trichlorhydrin, boiling at 155—157°, the last of these being only present in very small quantity. A. H.

Constitution of Salts of the Nitro-paraffins. By J. U. Nef (*Annalen*, 1894, **280**, 263—291).—The result of the author's experiments is to show that sodium nitroethane must be represented by the expression CHMe:NO·ONa, and not by the formula CHMeNa·NO_2; the addition of sodium ethoxide and subsequent elimination of water involved in its formation being comparable with the formation of ethylic sodiomalonate from ethylic malonate and sodium ethoxide. In support of this conclusion, the following is brought forward.

The free nitro-paraffins do not correspond in constitution with their salts; this is shown by the difficulty experienced in regenerating them from the salts by the action of acids. When a 10 per cent. solution of sodium nitroethane is quickly added to 20 per cent. sulphuric acid, a green coloration is produced, and heat is developed, accompanied by the liberation of acetaldehyde and nitrous oxide. Regeneration of nitroethane takes place only when dilute sulphuric acid is slowly added to a well-cooled solution of nitroethane in slight excess of caustic potash or sodium ethoxide, and even under these conditions the yield does not exceed 25 per cent. Similarly, nitroethane mercurichloride yields acetaldehyde and nitrous oxide, but no trace of nitroethane, when treated with acids; this observation is directly opposed to V. Meyer's statement that nitroethane is liberated from the mercuric salt by acids. The addition of dilute sulphuric or hydrochloric acid to the aqueous solution of sodium nitromethane gives rise to nitrous oxide, formaldehyde, nitrous acid, carbonic anhydride, and hydroxylamine; by keeping the temperature low, and adding the acid very slowly, about 25 per cent. of nitromethane may be recovered. The sodium salt of secondary nitropropane undergoes an analogous decomposition with formation of acetone and nitrous oxide.

The formation of a yellow, explosive mercuric salt, on adding sodium nitromethane to mercuric chloride solution, has been observed by V. Meyer and Rilliet (*Ber.*, **5**, 1030), who regarded it as mercuric nitromethane, but did not investigate it further. Analysis shows it to be free from hydrogen. The white precipitate, which is first formed on mixing the solutions, consists most probably of the unstable mercuric nitromethane, and this, immediately losing water, becomes converted into mercuric fulminate, which may be obtained in quantities amounting to 20 per cent. of the sodium nitromethane employed. There is every probability that the yellow precipitate described by V. Meyer and Rilliet consists of *basic mercuric oximidocarbonate*, $(Hg<^{O}_{O}>C{:}NO)_2Hg$, which forms an insoluble residue from which the solution of mercuric fulminate may be filtered. The salt explodes very readily, but may be cautiously dried at 100°; it is

unchanged by dilute nitric or sulphuric acid, but with hydrochloric acid, it yields mercuric chloride, carbonic oxide, and a substance having the odour of hydrogen cyanide. It is decomposed by strong hydrochloric acid into carbonic anhydride and hydroxylamine.

Dinitroethane is best prepared by agitating for 24 hours a mixture of 50 grams of bromonitroethane, 50 c.c. of alcohol, and 56 grams of potassium nitrite dissolved in 56 c.c. of water; potassium dinitroethane separates out slowly, and may be converted into the silver salt by mixing its solution with silver nitrate. When silver dinitroethane is allowed to fall into twice its weight of methylic iodide, silver iodide is at once precipitated, and the odour of formaldehyde becomes perceptible (compare Duden, Abstr., 1894, i, 101). By suitable treatment, the liquid may be made to yield dinitroethane, ethylnitrolic acid, β-dinitropropane, and an oil which is most probably the ethylic salt of ethylnitrolic acid. The *benzoic* derivative of this acid forms colourless needles which melt at 135°. Silver dinitromethane is also decomposed when thrown into five parts of ethylic iodide, acetaldehyde, ethylnitrolic acid, dinitroethane, and an oil, which is most probably β-dinitrobutane, being formed.

M. O. F.

Oil of Pelargonium from Reunion. By P. Barbier and L. Bouveault (*Compt. rend.*, 1894, **119**, 281—284).—When crude oil of pelargonium from Reunion is saponified with alcoholic potash and then fractionated, the principal fraction boiling at 115—116° is a colourless oil with an odour of roses; sp. gr. at 0° = 0·8866; observed rotation in column 200 mm. long = −12° 28′. The authors call it provisionally *pelargonium rhodinol;* with acetic anhydride, it yields an *acetate* which boils at 120° under a pressure of 10 mm., and which, when saponified, regenerates rhodinol with a somewhat lower sp. gr., 0·8826, and a rotatory power of −7° 12′. This substance is under investigation.

The fraction boiling at 80—100° closely resembles licareol. When treated with acetic anhydride, it yields a considerable proportion of a hydrocarbon boiling at 60—80° in a vacuum, and an acetate boiling at about 120°; but about half the product is unchanged even in presence of excess of acetic anhydride, and this portion, boiling at 90—95°, is a mixture of two ketones, one saturated and identical or isomeric with menthone, $C_{10}H_{18}O$, and the other, $C_{10}H_{16}O$, unsaturated. The constitution of the latter has not yet been ascertained, but the mixture of the two, when oxidised, yields large quantities of acetone, and of β-methyladipic acid melting at 84°. The alcohol which accompanies these ketones is licareol, and the alcohol regenerated from the acetate is identical with licarhodol.

The acids present in the crude oil of pelargonium as ethereal salts are acetic, isobutyric, isovaleric, and tiglic acids, and a small quantity of an acid, probably $C_9H_{15}\cdot COOH$, boiling at 250°.

There is also present a dark blue liquid which boils at about 165—170° under a pressure of 10 mm., and seems to be the ether $(C_{10}H_{17})_2O$; a small quantity of a substance resembling the stearoptene of roses is likewise present.

C. H. B.

Acetol Ethyl Ether and the Formation of Epiethylin. By A. Peratoner (*Gazzetta*, 1894, **24**, ii, 36—44).—The author has not obtained satisfactory results in the preparation of acetol ethyl ether, $CH_2Ac{\cdot}OEt$, by using Erlenbach's method (Abstr., 1892, 953); the hydrogen chloride liberated during the distillation acts on the product. On turning to Kutscheroff's process, namely, the action of freshly prepared mercuric bromide on ethylic ethylpropargylate suspended in water, it was found that when the ethylic salt was treated with an excess of somewhat impure mercuric bromide in presence of water, violent ebullition occurred, and ethylic alcohol was the only product which could be isolated; on using less mercuric bromide and warming on the water bath, ethyl glycide ether (epiethylin) was obtained. The latter has the normal molecular weight in boiling acetic acid, and was identified by its boiling point and by its yielding ethyl chlorhydrin when dissolved in hydrochloric acid. The author is unable to say what impurity in the mercuric bromide caused the action to proceed in the way mentioned above.

Acetol ethyl ether is best prepared by agitating ethylic ethylpropargylate with a saturated solution of mercuric chloride; a white *substance*, $2C_5H_8O_2,3HgCl_2,3HgO$, falls, and yields the ether on distillation with hydrochloric acid and subsequent treatment of the distillate with sodium carbonate. With sodium hydrogen sulphite, the ether yields a *compound*, $C_5H_{10}O_2,NaHSO_3$, crystallising in long, prismatic needles. The *oxime* of the ether, $C_5H_{10}O_2N$, is obtained as an oil boiling at 185—190°; the *acetoxime* boils at 188°, has an odour much resembling that of acetoxime, and is hydrolysed by heating with dilute hydrochloric acid.

Acetol ethyl ether boils at 129° under 759·5 mm. pressure (corr.), and has the sp. gr. 0·9562 at 0° and 0·8497 at 99·97°. Ethyl glycide ether boils at 128° under 760 mm. pressure, and has the sp. gr. 0·9635 at 0° and 0·8277 at 99·97°.

Acetylene forms a *mercuric* compound of the composition

$$C_2H_2,3HgCl_2,3HgO.$$

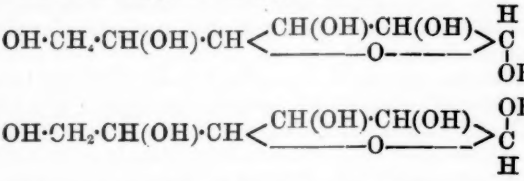
W. J. P.

The Second Methylglucoside. By W. A. van Eckenstein (*Rec. Trav. Chim.*, 1894, **13**, 183—186).—When preparing methylglucoside by E. Fischer's method (Abstr., 1894, i, 4), the author noticed that the rotatory power of the hydrochloric acid solution increased, and he was thus led to suspect the presence in this solution of a lævorotatory methylglucoside, which was gradually undergoing a transformation into the dextrorotatory variety. By using a more dilute (28 per cent.) solution of hydrogen chloride in methylic alcohol, and acting with this on glucose, the acid being neutralised as soon as the solution ceased to reduce Fehling's solution, he obtained a mixture of the two isomeric methylglucosides in about equal proportions, and on crystallising this mixture he found that the *lævorotatory methylglucoside* was first deposited. This crystallises in octahedra, which contain $\frac{1}{2}H_2O$; melts when anhydrous at 104°; is more soluble in alcohol and less so in water than its dextrorotatory isomeride, and is much more readily hydrolysed by acids. C. F. B.

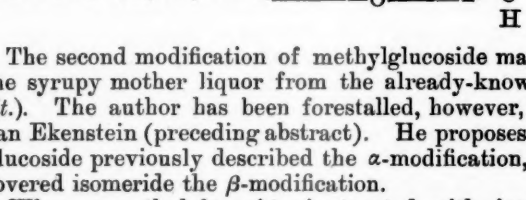
Influence of Configuration on the Action of Enzymes. By E. FISCHER (*Ber.*, 1894, **27**, 2985—2993).—Fischer and Thierfelder (Abstr., 1894, i, 486) put forward the hypothesis that the active chemical agents of the yeast cells can only attack those sugars which have a similar configuration. The present experiments show that the action of the two enzymes, invertase and emulsin, on these substances is likewise dependent on the molecular configurations of the compounds dealt with.

Invertase.—The experiments with this enzyme were made with the filtered extract obtained by digesting 1 part of air-dried beer-yeast (Frohberg type) with 15 parts of water for 15 hours at 30—35°.

The formula proposed by the author for the glucosides of the alcohols (Abstr., 1894, i, 4) renders possible the existence of two stereoisomerides having the configurations



and



The second modification of methylglucoside may be obtained from the syrupy mother liquor from the already-known modification (*loc. cit.*). The author has been forestalled, however, in its isolation, by van Ekenstein (preceding abstract). He proposes to call the methylglucoside previously described the α-modification, and the newly-discovered isomeride the β-modification.

When α-methylglucoside is treated with invertase at 30—35°, about half is hydrolysed at the end of 20 hours, whilst the β-modification remains unaltered under these circumstances. This fact is the more remarkable, seeing that van Ekenstein has observed that the β-modification is more readily hydrolysed by dilute acids than the α-modification. Crystallised ethylglucoside (Abstr., 1894, i, 565) is hydrolysed by invertase, and therefore belongs probably to the α-series. Benzyl- and glyceryl-glucosides have, as yet, only been obtained in the amorphous condition, but inasmuch as they are hydrolysed much less completely than the pure α-glucoside, they are probably mixtures of the α- and β-modifications. Methyl- and ethyl-galactosides, methyl-, ethyl-, and benzyl-arabinosides, and methyl- and ethyl-rhamnosides are not attacked by invertase: the five first compounds are crystalline, and are probably the β-modifications. Methyl-*l*-glucoside, probably the α-modification, was obtained as a syrup; the action of invertase gave a negative result.

The author finds that yeast extract readily and completely effects the conversion of maltose into glucose, although commercial solid invertase is without action on this sugar, as it is, also, on α-methylglucoside. Whether the enzyme which effects this change is identical with the so-called glucase of maize cannot, at present, be ascertained. Contrary to Dastre's observation (*Compt. rend.*, **96**, 932), the enzyme of yeast is without action on milk sugar. The author, there-

fore, regards maltose and milk sugar as related to one another in the same way as methylglucoside is to methylgalactoside.

Inulin and starch are not hydrolysed by invertase, neither are salicin, coniferin, phloridzin, or Michael's synthetical phenolglucoside (*Compt. rend.*, **89**, 355). A solution of invertase hydrolyses amygdalin readily with the formation of glucose, but neither benzaldehyde nor hydrogen cyanide are produced, so that its action is quite different from that of emulsin.

Invertase solution rapidly undergoes putrefactive change, but this may be prevented by the addition of chloroform, which does not influence its hydrolytic action. An addition of $2\frac{1}{2}$ per cent. of phenol, however, completely arrests the action of invertase. The extract obtained from yeast of the Saaz type behaves in the same way towards the glucosides of the alcohols and maltose as that from the Frohberg type. The enzyme from milk-sugar yeast does not, however, hydrolyse maltose, and the same is to be expected of *Saccharomyces exiguus Ludwigii* or *apiculatus*.

Emulsin.—The experiments were carried out at 30—35°, with 1 part of this enzyme to 2 parts of the glucoside and 20 parts of water, the action being maintained for 15—20 hours. Amongst the glucosides of the alcohols, only the derivatives of *d*-glucose appear to be hydrolysed by emulsin, but in contradistinction to the action of invertase, β-methylglucoside, and not the α-modification, is hydrolysed. Maltose and saccharose are not appreciably attacked by emulsin, although this enzyme hydrolyses milk sugar.

Enzyme of Kephir grains.—The author was unable to test the action of the enzyme of milk-sugar yeast on milk sugar itself on account of lack of this yeast. He finds, however, that an aqueous extract of kephir grains hydrolyses milk sugar.

The paper concludes with a theoretical discussion on the influence of the geometrical configuration of glucosides on the action of enzymes.

A. R. L.

Maltose and its Anhydride. By C. A. Lobry de Bruyn and F. H. van Leent (*Rec. Trav. Chim.*, 1894, **13**, 218—222).—Maltose loses 1 mol. of water and forms an anhydride when it is heated at 130—135°, or in a vacuum at 105°, or when it is boiled with absolute alcohol. The anhydride readily absorbs water, maltose being re-formed; its specific rotation $\alpha_D = 140{\cdot}7°$, but after 24 hours it becomes 137·7°; it yields the same phenylosazone as maltose itself. C. F. B.

Formation of Pentosans in Plants. By G. de Chalmot (*Ber.*, 1894, **27**, 2722—2725).—Pentoses are not direct products of the process of assimilation in plants, and, therefore, must be formed from hexoses. Now xylosans are always associated with celluloses containing glucose-groups, and arabinose with substances containing galactose-groups. And if E. Fischer's stereometric formulæ of *d*-glucose and *d*-galactose be compared with those of *l*-xylose and *l*-arabinose, it will be seen that the two latter can be derived respectively from the two former by oxidising the end group, $CH_2{\cdot}OH$, which these contain, and replacing it by H. For this it would be necessary that the CHO-group should be protected from oxidation, as might be the case if the

molecule had formed condensation products with other molecules. And so it seems probable that complex molecules containing pentose-groups are formed by the oxidation of complex molecules containing hexose-groups. C. F. B.

Properties and Reactions of Pectous Substances. By L. MANGIN (*Bied. Centr.*, 1894, **23**, 547—548; from *Jour. de Bot.*, 1892, 206, 235, and 363).—Pectous substances are divided into: (1) Pectose, which occurs with cellulose, and is insoluble in water and in copper ammonium hydroxide, but is dissolved by alkalis. (2) Pectin, which readily gelatinises in water and is not precipitated by lead acetate. (3) Parapectin, obtained by prolonged boiling from pectin; it is precipitated by lead acetate. (4) Metapectin, produced by boiling parapectin with dilute acids; it is precipitated by barium chloride. (5) Pectic acid, insoluble in water, alcohol, and acids; the alkaline salts are soluble, but not those of the alkaline earths. The acid is also soluble in alkaline carbonates and phosphates, and in the ammonium salts of organic acids, forming, it is supposed, double salts. When the acid is boiled with alkalis, metapectin (? metapectic acid) is formed. This is quite insoluble in water, and forms soluble salts with all bases, including calcium and barium. The metapectates become yellow in presence of an excess of alkali. Metapectic acid is converted by sulphuric acid into arabinose and another substance not further examined.

Pectous substances yield mucic acid when heated with dilute nitric acid. They are not coloured blue or violet by iodine. They occur in all plants (except some fungi), and in all membranes except those which have become woody. N. H. M.

Selenitines. By G. CARRARA (*Gazzetta*, 1894, **24**, ii, 173—179).—The author has succeeded in preparing a new class of selenium compounds, to which he gives the name selenitines; they are thetines, in which selenium takes the place of sulphur.

Diethylselenitine bromide, $SeEt_2Br\cdot CH_2\cdot COOH$, is prepared by warming ethylic selenide with fused bromacetic acid; the action is complete in a day, and the bromide is obtained in deliquescent prisms, melting at 74°. It is soluble in water or alcohol, but insoluble in ether, and has an acid reaction. *Diethylselenitine platinochloride*, $(C_6H_{12}O_2Se)_2,H_2PtCl_6$, may be prepared by a process similar to that used in preparing the platinochlorides of the thetines (Abstr., 1893, i, 633); it is crystalline, and melts and decomposes at 150—151°. The corresponding *hydroxide*, $OH\cdot SeEt_2\cdot CH_2\cdot COOH$, is obtained by the action of moist silver oxide on the bromide; it is a deliquescent, crystalline substance, having an acid reaction.

On treating the dibromide of diethylic selenide, $SeEt_2Br_2$, with sufficient silver acetate to eliminate one-half of the bromine, and evaporating the solution, a product is obtained, consisting of white, deliquescent needles. This, after treatment with silver chloride, yields, with platinic chloride, the *ethylic platinochloride* of diethylic selenide, $(SeEt_2)_2,Et_2PtCl_6$. The corresponding *methylic platinochloride*, $(SeEt_2)_2,Me_2PtCl_6$, crystallises in laminæ. W. J. P.

Mercuric Formamide. By B. Fischer and B. Grützner (*Arch. Pharm.*, 1894, **232**, 329–333).—Recently prepared mercuric oxide dissolves in formamide, and, on treatment with alcohol, *basic mercuric formamide*, HCO·NH·Hg·OH, is precipitated; it is a colourless powder, which is decomposed when heated above 35°, and at ordinary temperatures by the action of light; it dissolves in dilute hydrochloric acid and in formamide, and is decomposed when heated with potash, ammonia being evolved; the mercury is only incompletely precipitated by hydrogen sulphide. By the action of hydrochloric acid on the preceding compound, the *chlorides*, $(HCO·NH·HgCl)_2 3HCl$ and HCO·NH·HgCl,HCl, are formed, the former with dilute, the latter with concentrated, acid; both are crystalline, have an acid reaction, and precipitate albumin, but cease to do so and become neutral by treatment with sodium chloride. With potash, the former, which is the more soluble, gives a pale yellow, the latter a greyish-yellow precipitate, and, on boiling, ammonia is evolved.

J. B. T.

Bivalent Carbon. By J. U. Nef (*Annalen*, 1894, **280**, 291—342; compare Abstr., 1892, 1438).—The author has accumulated more evidence in support of his opinion that isocyanides contain bivalent carbon, having studied methylic and ethylic isocyanides on the lines already indicated in the investigation of the analogous aromatic compounds.

Methylimidobenzoylformic acid, NMe:CBz·OH, is obtained by heating a mixture of methylic isocyanide with benzoic chloride, in molecular proportion, for half an hour at 100°; it forms heavy, pale yellow crystals, which melt at 74°. The solution in dilute caustic soda yields an oily hydrate when acidified, together with what is probably a polymeric modification of the original substance. The *phenylhydrazone hydrate* is produced by combination with phenylhydrazine in ethereal solution; it is insoluble in water, and is not decomposed by cold caustic soda, but, when warmed for half an hour with the latter, methylamine is eliminated, and the phenylhydrazone of benzoylformic acid formed; this melts at 163° (Elbers found 153°).

Ethylic isocyanide undergoes molecular rearrangement when heated for three hours at 230—255°, propionitrile being formed almost quantitatively. Heated for two hours at 110—120° with sulphur dissolved in carbon bisulphide, it is converted into ethylthiocarbimide.

Ethylimidothioformic acid, NEt:CH·SH, is prepared by heating, for four hours at 100°, a mixture of ethylic isocyanide and alcohol saturated with hydrogen sulphide. It is a yellow oil, which boils at 125° (14 mm.); its taste is bitter, and it dissolves in water slowly, but is more readily soluble in dilute caustic soda.

Isocyanoethylic dichloride (*ethylimidocarbonyl chloride*), $NEt:CCl_2$, is produced on passing chlorine over the surface of a solution of ethylic isocyanide in chloroform kept at −19°; a better method of preparation consists in adding sulphuryl chloride to a solution of ethylic isocyanide in ether at −15°. It is a colourless oil, which boils at 102°.

Ethylimidopyruvic phenylhydrazone, NEt:C(OH)CMe:N·NHPh, is obtained by the interaction of ethylic isocyanide and acetic chloride; the product, after remaining for 12 hours at the ordinary temperature,

is mixed with water at 0° and treated with phenylhydrazine. The hydrazone melts at 165°, and is insoluble in water and alkalis. If, previous to decomposition with water, the product be distilled under 15 mm. pressure, a yellow oil passes over at 50—60°, the boiling point of which is 100—130° at atmospheric pressure. It consists of *ethylimidopyruvic chloride*, NEt:CCl·COMe, but, as it undergoes partial decomposition when boiled, it could not be obtained pure. The ease with which this and many additive compounds of the isocyanides undergo dissociation, coupled with the violent character of the action during their formation from the constituents, suggests a parallel between bivalent carbon compounds and those of trivalent nitrogen.

Carbonyl chloride unites with ethylic isocyanide at −15° with explosive violence, which is somewhat moderated by the employment of ether as a diluent; the product, however, decomposes when boiled at reduced pressure, and was not further investigated. Ethylic chlorocarbonate forms an additive compound, which dissociates at 100° into carbonic anhydride, ethylic chloride, and ethylic isocyanide, the latter at once becoming polymerised. That the intermediate imidochloride, NEt:CCl·COOEt, is first formed, is shown by the production of ethylic oxamate when the crude product is warmed with lime-water, after polymerised ethylic isocyanide and the ether employed in the operation have been removed.

From the foregoing experiments, it will be seen that the aliphatic isocyanides differ from those of the aromatic series only in their greater chemical activity. In addition to the substances already mentioned, ethylic isocyanide reacts with carbon tetrachloride at 180°, with benzenesulphonic chloride at 85°, and with benzylic chloride at 120°, but the products do not invite further investigation. It is remarkable that ethylic isocyanide and sodium ethoxide may be heated together for an hour at 130—170° without action taking place.

The author advances the view that fulminic acid contains bivalent carbon, and is to be represented by the formula C:NOH. This is rendered probable by the synthesis of mercuric fulminate from sodium nitromethane (this vol., i, 3), and further light is thrown on the question by the contradiction of the statement that hydrogen cyanide is formed when fulminates are decomposed by hydrochloric acid. If this acid, mixed with the same volume of water, is added to the aqueous solution of sodium fulminate at 0°, and the mixture at once extracted with ether, an ethereal solution of *chloro-formoxime*, CHCl:NOH, is obtained, and on cautious removal of the solvent at 0°, the substance is deposited in long, transparent, colourless needles; it is also formed when silver fulminate is added to hydrochloric acid at 0°. The substance, in the solid state and also in concentrated ethereal solution, remains unchanged at 0°, but it spontaneously decomposes at ordinary temperatures with production of a green coloration accompanied by development of great heat and emission of a hissing sound; carbonic oxide is eliminated, and the yellowish residue consists chiefly of hydroxylamine hydrochloride. Chloroformoxime is very poisonous, and has a pungent odour which strongly resembles that of hydrogen cyanide when the vapour is diluted with air; this observation explains the erroneous conclusion that hydrogen

cyanide is formed when fulminic salts are decomposed by hydrochloric acid. Inhaled in small quantities, it induces salivation, laryngital irritation and violent headache, whilst the eyes become painfully inflamed a few hours after exposure to the vapour. The substance is not attacked by water and alcohol; with silver nitrate, it yields silver fulminate, which may be removed in the form of its double salt, C:NOAg,C:NOK, by extraction with potassium chloride. When silver fulminate is treated with dilute hydrochloric acid at 0° (1 mol.), a mixture of chloro-formoxime and its *silver* salt,

$$CHCl{:}NOAg,$$

is produced (compare Ehrenberg, Abstr., 1885, 38). The latter remains in aqueous solution after extraction with ether, and the addition of hydrochloric acid precipitates silver chloride, which is mixed with silver fulminate if nitric acid is used. This case of a silver salt retaining the metal unattacked in contact with hydrochloric acid is comparable with the behaviour of ethylic sodacetoacetate in the presence of alkyl halogen compounds.

Hydrogen sulphide effects an analogous decomposition of silver fulminate with formation of *silver thioformohydroxamate*,

$$SH{\cdot}CH{:}NOAg;$$

with silver nitrate, the aqueous solution of this yields silver sulphide and fulminate, and silver sulphide and chloride with hydrochloric acid.

Phenylisuretine, NPh:CH·NH·OH, is formed when chloro-formoxime in ethereal solution is mixed with aniline. It was identified by comparing it with the product obtained from isuretine and aniline hydrochloride. Melting at 138°, it dissociates into phenylic isocyanide and hydroxylamine, a decomposition which is also effected by dilute caustic soda.

Cyanisonitrosoacetohydroxamic acid, HON:C(CN)·C(OH):NOH, is obtained by agitating an ethereal solution of chloro-formoxime with small quantities of ammonia until the odour of the latter remains. The acid, formed by decomposing the ammonium salt with dilute hydrochloric acid, crystallises from ether in colourless cubes, which melt and decompose at 117—118°. The *monosilver* salt, $C_3H_2N_3O_3Ag$, forms flat, yellow prisms, and the *dipotassium* salt, $C_3HN_3O_3K_2 + H_2O$, was obtained as a crystalline powder. The action of excess of ammonia on cyanisonitrosoacetohydroxamic acid gives rise to the three substances $C_3H_4N_4O_2$, $C_3H_3N_3O_3$, and a syrup yielding the crystalline ammonium salt of the formula $C_3H_7N_5O_3$, all isolated by Ehrenberg from chloro-formoxime by treatment with aqueous ammonia (*loc. cit.*); the two latter substances are also obtained by heating the aqueous solution of the acid for two hours on the water-bath.

Caustic potash eliminates ammonia from cyanisonitrosoacetohydroxamic acid, the potassium salt $C_3HN_2O_4K,H_2O$ being formed, whilst hydrochloric acid decomposes it into oxalic acid, carbonic anhydride, ammonium chloride, and hydroxylamine hydrochloride.

When ethylic cyanisonitrosoacetate is heated with alcoholic ammonia at 100°, deoxyfulminuric acid is formed (compare Seidel,

Abstr., 1892, 1117), and since cyanisonitrosoacetic acid is produced by hydrolysis of deoxyfulminuric acid, the latter must be identical with cyanisonitrosoacetamide.

Sodium ferrofulminate, $Na_4Fe(ON{:}C)_6 + 18H_2O$, is obtained by adding a solution of ferrous sulphate to sodium fulminate (6 mols.) containing a small quantity of caustic soda. On evaporating the liquid, yellow needles a centimetre long are deposited. The aqueous solution is unstable unless caustic soda is present, the liquid rapidly becoming purple; ferric chloride produces an intense purple-red coloration. Removal of the water of crystallisation from this salt involves its dissociation into sodium and ferric fulminates, whilst hydrochloric acid gives rise to chloro-formoxime. Ferric hydroxide and sulphide are produced by the action of caustic soda and ammonium sulphide respectively, and lead acetate, silver nitrate, and mercuric chloride precipitate the corresponding fulminates.

The chief products of the action of ethylic iodide on silver fulminate are ethylic cyanate and cyanurate; at the same time, the author regards the formation of ethylic carboxime C:NOEt, as probable.

Ethoxyformamidine, $NH_2{\cdot}CH{:}NOEt$, is obtained by the action of sodium ethoxide and ethylic iodide on isuretine. It forms a colourless oil which boils at 170—175°, and dissolves readily in water. The *platinochloride* crystallises in yellow quadratic plates, and melts at 153°. Nitrous acid converts ethoxyformamidine into an oil which is probably the ethylic derivative of chloro-formoxime.

M. O. F.

Carbonyl Nitride and Dicarbamide. By T. Curtius and K. Heidenreich (*Ber.*, 1894, **27**, 2684—2685).—*Carbonyl nitride*, $CO(N_3)_2$, is formed by the action of sodium nitrite on the hydrochloride of carbohydrazide, $CO(NH{\cdot}NH_2,HCl)_2$. It is an explosive oil, and when boiled with alcoholic aniline yields carbanilide and diazoimide, N_3H.

Dicarbamide (*bishydrazicarbonyl*), $CO<^{NH{\cdot}NH}_{NH{\cdot}NH}>CO$, is obtained by heating ethylic hydrazinedicarboxylate, $N_2H_2(COOEt)_2$, with hydrazine hydrate at 100°. It crystallises in monoclinic prisms, melts at 270°, and behaves like a monobasic acid; the *ammonium* and *barium* salts crystallise respectively with 1 and 3 H_2O; it, however, also yields a *diammonium* salt. It yields a *benzylidene* derivative, $C_2H_2N_4O_2{:}CHPh$, melting at 253°, and it is hydrolysed by strong hydrochloric acid at 150°, yielding carbonic anhydride and hydrazine.

Methenylcarbohydrazide, $CO<^{NH—N}_{NH{\cdot}NH}>CH$, is formed when ethylic orthoformate is heated with carbohydrazide at 100°. It melts at 181°, behaves like a feeble monobasic acid, and is hydrolysed by hydrochloric acid to carbohydrazide and formic acid. C. F. B.

Carbamide Derivatives of Tribromopyruvic acid. By C. Boettinger (*Arch. Pharm.*, 1894, **232**, 346—349).—Tribromopyruvic acid decomposes when boiled in aqueous solution; by the action of ammonia at the ordinary temperature, it is converted into oxalic acid,

bromoform, and a little carbonic anhydride, but only two-thirds of the oxalic acid indicated by the equation $CBr_3{\cdot}C(OH)_2{\cdot}COOH = CHBr_3 + C_2H_2O_4$ is produced. When intimately mixed with carbamide or thiocarbamide (2 mol.), it liquefies, and by treatment with alcohol and ether the *carbamide*, $C_4H_7Br_3N_2O_5$, is obtained; this crystallises in colourless prisms, melts and decomposes at 125°, yields bromoform when boiled with water, and by the action of ammonia is converted into bromoform, oxalic acid, and carbonic anhydride, the last two in molecular proportion. With silver nitrate and mercuric nitrate, white precipitates are formed; the *silver* salt is almost completely soluble in nitric acid; the *mercury* salt is not changed by soda. With concentrated sulphuric acid, the carbamide evolves hydrogen bromide and bromine; the *diureïde* is formed along with the carbamide, and may be separated from the latter, as well as from some unaltered acid, by taking advantage of its solubility in ether; it is deposited from water in small, colourless crystals, darkens at 182°, and melts at 198—199°. The *mercuric* salt is colourless, and not altered by soda; the *copper* salt is greenish-blue, and soluble in ammonia; the *silver* salt is colourless, and dissolves in ammonia or nitric acid, but, on heating, silver bromide is precipitated. J. B. T.

Thiohydantoïnacetic acid and Diphenylthiohydantoïnacetic acid. By R. Tambach (*Annalen*, 1894, **280**, 233—246).—*Thiohydantoïnacetic acid*, $\begin{matrix}NH{:}C & --- & S\\ | & & \\ NH{\cdot}CO & & \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}COOH$, is obtained by warming a mixture of thiocarbamide with bromosuccinic acid in molecular proportion. It separates from boiling water in slender, colourless prisms, which decompose without fusion at 210°. The aqueous solution is strongly acid, forming crystalline metallic salts; it also unites with hydrochloric acid. The *ammonium* salt forms colourless, hexagonal prisms, which contain $1H_2O$ and dissociate at 150°. The crystalline form is asymmetric, and the axial ratio $a : b : c = 0{\cdot}8833 : 1 : 0{\cdot}6359$. The *sodium* salt contains $3H_2O$, and the *lead* salt is anhydrous. The *hydrochloride* forms large needles which are decomposed by water; the *platinochloride* crystallises with $1H_2O$.

Diphenylthiohydantoïnacetic acid, $\begin{matrix}NPh{:}C & --- & S\\ | & & \\ NPh{\cdot}CO & & \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}COOH$, is prepared by boiling together alcoholic solutions of diphenylthiocarbamide and bromosuccinic acid, or by fusing a mixture of these substances in molecular proportion. When recrystallised from alcohol, it melts at 189—189·5°. Desulphurising agents are without action on this and the foregoing acids. The *ammonium* salt dissociates when dissolved in water, and the *hydrochloride*, which melts at 193—195°, exhibits the same property.

Dioxythiazoleacetic acid, $C_5H_5O_4NS$, is obtained from thiohydantoïnacetic acid by the action of boiling dilute hydrochloric acid. It forms monosymmetric prisms having the axial ratio $a : b : c = 2{\cdot}3449 : 1 : 0{\cdot}8936$. It melts at 168·5—169°.

Phenyldioxythiazoleacetic acid, $C_{11}H_9O_4NS$, is prepared by boiling diphenylthiohydantoïnacetic acid with dilute hydrochloric acid,

aniline being eliminated; it melts at 146—147°. The *silver* salt is decomposed by light and heat.

When thiohydantoïnacetic acid is hydrolysed by means of barium hydroxide, cyanamide and thiomalic acid are formed, whilst diphenylthiohydantoïnacetic acid, on similar treatment, gives rise to cyanamide and diphenylthiocarbamide. A characteristic reaction of thiomalic acid is the development of a deep blue coloration on the addition of dilute ferric chloride solution. M. O. F.

Condensation of Formaldehyde with Alcohols of the Fatty Series in presence of Hydrochloric acid. By C. FAVRE (*Compt. rend.*, 1894, **119**, 284—286).—A 40 per cent. commercial solution of formaldehyde is mixed with a slight excess of the particular acid, and a current of hydrogen chloride is passed through the mixture, which must be kept cool. After some time, the liquid separates into two layers, the lower of which, more or less strongly coloured, consists of water and the excess of alcohol saturated with hydrochloric acid. The upper layer is purified by fractionation.

The compounds, $CH_2Cl{\cdot}OR$, formed are more stable the higher the molecular weight. They fume in contact with air, and give off an odour of formaldehyde and hydrochloric acid. Water decomposes them, and regenerates formaldehyde, the alcohol, and hydrochloric acid; this action being slower the higher the molecular weight.

Wurtz and Frapoli obtained acetal by means of the reaction $CH_3{\cdot}CHCl{\cdot}OEt + EtONa = NaCl + CH_3{\cdot}CH(OEt)_2$, but the author finds that the same action takes place with the alcohol itself, and in this way he has prepared a series of mixed acetals $RO{\cdot}CH_2{\cdot}OR'$, which are under investigation.

In order to obtain the formals, the monochlorinated derivatives are heated with a slight excess of the alcohols, and then washed with concentrated sodium hydroxide solution to remove hydrochloric acid. The yield is higher, the higher the molecular weight. The same compounds have been obtained by Trillat and Cambier by a different method: their properties are summarised in the following table.

	Boiling point.	Sp. gr. 15°/4°.	Refractive index, n_{19}.
Chloromethyl ether, $CH_2Cl{\cdot}OMe$	59·5°	1·1508	1·389
Dimethylformal, $CH_2(OMe)_2$	45·5	0·872	1·356
Chloromethylic ethylic oxide, $CH_2Cl{\cdot}OEt$	80·0	1·023	1·401
Diethylformal, $CH_2(OEt)_2$	74·0	0·831	1·369
Chloromethylic propylic oxide, $CH_2Cl{\cdot}OPr$	112·5	0·985	1·409
Dipropylformal, $CH_2(OPr)_2$	140·5	0·827	1·391
Chloromethylic isobutylic oxide, $CH_2Cl{\cdot}OBu$	131·0	0·947	1·410
Diisobutylformal, $CH_2(OBu)_2$	164·5	0·837	1·400
Chloromethylic amylic oxide, $CH_2Cl{\cdot}OC_5H_{11}$	154·0	1·066	1·425
Diamylformal, $CH_2(OC_5H_{11})_2$	207·5	0·841	1·412

C. H. B.

Contraction of Aqueous Solutions of Acetone. By K. T. P. McElroy (*J. Amer. Chem. Soc.*, 1894, **16**, 618—620).—The acetone used in the experiments was bought as pure, and was further purified by boiling for three days over calcium chloride, and redistilling. The fraction finally used boiled at 56·4°. The method employed was to weigh a flask, add water, weigh, add acetone, re-weigh, shake and determine the specific gravity, first at 20°, and then, without refilling the bottle, at 25°. The weight of the mixture, divided by its specific gravity, gave the actual volume of the mixture at that temperature. The difference between this figure and that representing the sum of the volumes of the unmixed liquids, when divided by the latter figure, gave the percentage of contraction.

The results are tabulated. The contractions, which do not materially vary from each other at 20° or 25°, gradually increase with the amount of water until this reaches 49·9 per cent. After this there is a steady decrease. The highest and lowest percentages of contraction are, respectively, 4·089 (with 49·9 per cent. of water) and 0·861 (with 4·99 per cent. of water). L. de K.

Methyl Octyl Diketone. By M. Fileti and G. Ponzio (*J. pr. Chem.*, 1894, [2], **50**, 370—378).—When methyl nonyl ketone is treated with nitric acid, it is converted into dinitrononane, methyl octyl diketone, and nonylic acid. Methyl octyl diketone may be isolated from this mixture in the form of the dioxime, from which the free ketone has not yet been obtained in the pure state. It is a yellow liquid, boiling at about 120° under a pressure of 17 mm., and forms a yellow vapour. The *dioxime*, $NOH{:}CMe{\cdot}C(NOH)[CH_2]_6{\cdot}CH_2Me$, crystallises from dilute alcohol in lustrous plates, melting at 162°. When boiled with dilute sulphuric acid, it yields the *monoxime*, which may also be prepared from methyl nonyl ketone by the action of hydrochloric acid and amylic nitrite. This melts at 56° when prepared from methyl nonyl ketone; at 58° when obtained from the dioxime, and crystallises in nacreous plates, or sometimes in vitreous needles. In spite of the difference in melting point, the authors consider that the two products are identical. *Methyl octyl diketonehydrazoxime*, $N_2HPh{:}CMe{\cdot}C(NOH){\cdot}C_8H_{17}$, forms small, pale yellow prisms, melting at 91—92°. The *hydrazone* crystallises in flat, yellow needles, melts at 91—92°, and is much more stable than the hydrazoxime.

The constitution of the substance as a diketone and not as a ketoaldehyde follows from the decomposition which the monoxime undergoes when it is boiled with dilute sulphuric acid, acetic and nonylic acids being produced along with ammonia. A. H.

Chromium Formate. By C. Haeussermann (*J. pr. Chem.*, 1894, [2], **50**, 383—384).—This salt is formed when hydrated chromium oxide is dissolved in formic acid (sp. gr. 1·15—1·2), and crystallises in dull dark green matted needles. The air-dried salt has the composition $Cr(CHO_2)_3,2[Cr(CHO_2)_2{\cdot}OH] + 4\frac{1}{2}H_2O$, loses water when preserved over sulphuric acid, and, when heated at 100—110°, has the composition $Cr(CHO_2)_3,[Cr(CHO_2)_2{\cdot}OH] + 1\frac{1}{2}H_2O$. A. H.

α-Bromopropionic acid. By M. Weinig (*Annalen*, 1894, **280**, 247—252).—The salts of α-bromopropionic acid are more easily decomposed by water than those of bromacetic acid. The *magnesium* salt contains $1H_2O$, the *calcium* salt crystallising with $2H_2O$; the *lead* and *copper* salts are anhydrous. The *methylic* salt boils at 140—150°, and its sp. gr. is 1·499 at 21°/4°; the ethylic salt boils at 159·4—160·2°, and has a sp. gr. = 1·4412 at 21·5°/4°; the *isoamylic* salt boils at 210—220°. M. O. F.

αβ-Dibromisovaleric acid. By M. Ariff (*Annalen*, 1894, **280**, 259—262).—αβ-Dibromisovaleric acid melts at 107·5—108°; its salts are very unstable. When the aqueous solution of the sodium salt is boiled, bromobutylene, $CMe_2{:}CHBr$, is formed; this is a colourless oil which boils at 91°, and is identical with Butlerow's bromisobutylene.

Bromobutylene dibromide, $CBrMe_2{\cdot}CHBr_2$, is obtained by the addition of bromine to the foregoing substance. It boils at 205—206°, and has sp. gr. = 2·0169 at 20°/4°. M. O. F.

Constitution of Oxybehenic acid. By M. Fileti and G. Baldracco (*J. pr. Chem.*, 1894, [2], **50**, 378—379; compare Abstr., 1894, i, 13).—When monochlorerucic acid is treated with concentrated sulphuric acid, an oxybehenic acid is obtained which is identical with that prepared by a similar process from chlorobrassidic acid. It follows from this that oxybehenic acid is a ketonic acid, and does not possess the structure of an anhydro-acid, in which case the two methods of preparation would have yielded different products. A. H.

Action of Hydrocyanic acid on Unsaturated Aldehydes. By G. Johanny (*Monatsh.*, 1894, **15**, 415—427; compare Abstr., 1891, 37; Lobry de Bruyn, Abstr., 1885, 242; 1886, 224).—On heating α-hydroxy-β-propylidenebutyramide with baryta, the barium salt of α-hydroxypropylidenebutyric acid, $(C_7H_{11}O_3)_2Ba + 3H_2O$, is obtained. It dissolves readily in water, from which it crystallises in rhombic prisms, $a : b : c = 1·0296 : 0·9369 : 1$. It is almost insoluble in alcohol, and, on treatment with an equivalent quantity of sulphuric acid, gives *α-hydroxy-β-propylidenebutyric acid*; this crystallises in deliquescent white scales and melts at 43°. The acid in chloroform solution gradually absorbs bromine, and is converted into the *dibromide*, $C_7H_{12}O_3Br_2$, which crystallises in triclinic prisms, $a : b : c = 1·2923 : 1·7737 : 1$, melts at 124—125°, and on treatment with dilute alkali forms methylethylacraldehyde, sodium formate, and the bromolactone, $C_7H_{11}O_3Br$; the latter crystallises in monoclinic plates $a : b : c = 0·7938 : 0·6788 : 1$, and melts at 82—83°. On reduction with hydriodic acid, α-hydroxy-β-propylidenebutyric acid is first converted into the hexylic iodide, $CH_2Et{\cdot}CMe_2I$, and finally forms the hexane, $CH_2Et{\cdot}CHMe_2$ (compare Wurtz, *Jahresb.*, 1855, 574). G. T. M.

Unsaturated acids. By R. Fittig (*Ber.*, 1894, **27**, 2658—2683).—A lecture delivered before the German Chemical Society, giving a chronological survey of the conclusions arrived at in this field. M. O. F.

Dimethylacrylic acid. By M. WEINIG (*Annalen*, **280**, 252—258).—Diethylaniline is a satisfactory agent for the elimination of hydrogen bromide from such substances as undergo further change by the action of aniline. Dimethylacrylic acid may be prepared in large quantities by boiling together ethylic α-bromisovalerate with diethylaniline for 5—6 hours in a reflux apparatus; the ethylic salt, which boils at 151°, is then hydrolysed by means of alcoholic potash. The *cadmium* salt melts and decomposes at 165°; it crystallises with $2H_2O$. The anhydrous copper salt is green. M. O. F.

Ethylenic Salts of Glycollic and Oxalic acids; Anhydrides of α-Halogen Fatty Acids. By C. A. BISCHOFF and P. WALDEN (*Ber.*, 1894, **27**, 2939—2952).—The following ethylenic salts were prepared in order to study their analogy to certain piperazine derivatives from which they differ by the substitution of oxygen for the group NPh (Abstr., 1893, i, 54). The *ethylenic salt of glycollic acid*, $O<\begin{matrix}CH_2\cdot CH_2\\CH_2-CO\end{matrix}>O$, may be prepared by acting on monosodioglycol with ethylic chloracetate suspended in benzene. It crystallises in prisms, or long, thin needles, melts at 31°, and boils at 214° under a pressure of 750 mm. *Ethylenic oxalate*, $O<\begin{matrix}CH_2\cdot CH_2\\CO-CO\end{matrix}>O$, is obtained by distilling a mixture of monethylic oxalate with glycol under a pressure of 5 mm. It forms white crystalline granules, melts at 142—143°, and boils at 196—198° under a pressure of 5 mm. When heated under the atmospheric pressure, carbonic oxide and carbonic anhydride are evolved.

The anhydrides of the α-halogen fatty acids are best prepared by distilling the acid with phosphoric anhydride.

Chloracetic anhydride, $(C_2H_2ClO)_2O$, boils at 109—111° under a pressure of 10 mm., and solidifies in colourless prisms, melting at 46°. Water gradually converts it into the acid. When treated with potassium carbonate, it is converted into the polyglycollide,

$$O<\begin{matrix}CH_2\cdot CO\\CO\cdot CH_2\end{matrix}>O.$$

α-Bromopropionic anhydride boils at 120° (5 mm.), and when treated with potassium carbonate yields the *lactide*, $O<\begin{matrix}CHMe\cdot CO\\CO\cdot CHMe\end{matrix}>O$, which melts at 124—125°.

α-Bromobutyric anhydride boils at 148—152° (10 mm.), and when treated with potassium carbonate yields the inner anhydride of α-hydroxybutyric acid, $CHEt<\begin{matrix}CO\cdot O\\O\cdot CO\end{matrix}>CHEt$. *α-Bromisobutyric anhydride* boils at 135—140° (35 mm.), melts at 63—65°, and crystallises in plates. Its behaviour towards potassium carbonate is abnormal, methacrylic acid being formed (compare Abstr., 1894, i, 496). A. H.

Ethylenic Salts of Bibasic Acids and Phenols. By D. VORLÄNDER (*Annalen*, 1894, **280**, 167—206).—The author's experiments

point to the probable existence of a connection between the nature of an ethylenic salt and the structure of the acid from which it is derived. Thus, whilst ethylenic carbonate has the constitution $CO<^{O\cdot CH_2}_{O\cdot CH_2}$, ethylenic succinate is best represented by the formula

$$\begin{matrix} CH_2\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH_2 \\ | \qquad\qquad\qquad\qquad\qquad\qquad | \\ CH_2\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH_2 \end{matrix}$$

This is indicated by a determination of the molecular weight, and by its formation from silver succinate and bischlorethylic succinate.

Ethylenic succinate prepared by heating succinic acid with glycol is identical with the product obtained from silver succinate and ethylenic bromide, or from succinic chloride and disodioglycol. It is readily soluble in chloroform, phenol, and hot nitrobenzene, less freely in acetone, benzene, and boiling alcohol; it separates from the last-named solvent in small, colourless crystals, which melt at 88—90°; when resolidified, it has a sp. gr. = 1·345 at 17°. It is not attacked by benzoic chloride, acetic anhydride, or the alkali carbonates, but hydrolysis is induced by hot caustic alkalis, the corresponding succinate being formed; ethylenic bromide and succinic acid result from the action of hydrobromic acid at 100°. Ammonia gives rise to succinamide, and with phenylhydrazine, succinylphenylhydrazide is obtained. Sodium ethoxide converts the ethylenic salt into ethylic succinosuccinate.

Ethylic chlorethylic succinate, $COOEt\cdot CH_2\cdot CH_2\cdot COO\cdot CH_2\cdot CH_2Cl$, is obtained by the action of succinic chloride on glycol at 70—80°; it boils at 170—172° (30 mm.). *Bischlorethylic succinate*,

$$C_2H_4(COO\cdot CH_2\cdot CH_2Cl)_2,$$

which is formed at the same time, boils at 204—205° (30 mm.). It is also produced when succinic chloride acts on ethylene chlorhydrin.

Ethylic hydroxyethylic succinate, $COOEt\cdot CH_2\cdot CH_2\cdot COO\cdot CH_2\cdot CH_2\cdot OH$, is obtained on heating ethylic succinate with glycol for 15 hours; it boils at 182—183° (25 mm.).

Ethylenic fumarate, $(C_6H_6O_4)_2$, is obtained by heating silver fumarate with ethylenic bromide for many hours. It melts at 109—110°, and when heated at 150—160° for five hours is converted into a transparent, insoluble, glass-like substance. Ethylenic fumarate is hydrolysed by caustic soda and barium hydroxide, whilst aqueous ammonia converts it into fumaramide. *Ethylenic dibromosuccinate*, $(C_6H_6O_4Br_2)_2$, is formed by the addition of bromine to ethylenic fumarate; it melts at 96°.

Bischlorethylic fumarate, $C_8H_{10}O_4Cl_2$, is obtained by warming a mixture of fumaric chloride and ethylene chlorhydrin. It crystallises in lustrous plates which melt at 71°. Conversion into ethylenic fumarate takes place on treating it with silver fumarate.

Ethylenic maleïnate corresponds in preparation and properties to the fumarate. It cannot be crystallised, and when treated with bromine in ethylenic bromide solution, it yields *ethylenic isodibromosuccinate*, which melts about 80°. *Ethylenic diphenylmaleïnate* melts at 112°; it has the formula $C_{12}H_{14}O_4$.

When the solution of ethylenic maleïnate in chloroform or glacial acetic acid is heated at 170° for 4—5 hours, it undergoes molecular rearrangement with formation of the *isomeride* $(C_6H_6O_4)_2$, which melts at 90—92°; ethylenic fumarate does not undergo this change. The maleïnate, when hydrolysed with barium hydroxide, yields barium fumarate. The *dibromo*-additive compound melts at 80—82°. When sodium amalgam is added to a solution of ethylenic fumarate or maleïnate in glacial acetic acid, reduction takes place, and ethylenic succinate is formed; this is also obtained by the interaction of bischlorethylic succinate and silver succinate.

Bromacetic bromide acts on glycol at 50—60° with formation of *β-bromethylic bromacetate*, $CH_2Br{\cdot}COO{\cdot}CH_2{\cdot}CH_2Br$, which boils at 147—148° (30 mm.); *ethylenic bisbromacetate*, $(CH_2Br{\cdot}COO)_2C_2H_4$, is produced at the same time; it boils at 205—206° (30 mm.).

Ethylenebisquinol, $C_2H_4(O{\cdot}C_6H_4{\cdot}OH)_2$, is obtained on heating a mixture of quinol and ethylenic bromide with sodium dissolved in absolute alcohol, in closed vessels at 95—100° for five hours; the alkaline mixture is acidified with acetic acid, and the crystalline solid thus obtained is extracted with dilute caustic soda. On adding an acid to this solution, the compound is thrown down, and may be recrystallised from dilute alcohol; it melts at 219—220°, and reduces Fehling's solution when boiled with it. The *diacetyl* derivative melts at 137—138°; the *diethylic* salt at 149°. Interaction with bromacetic bromide gives rise to the *bisbromacetyl* derivative, $C_{18}H_{16}O_6Br_2$, which forms long, lustrous plates, and melts at 156°. The portion of the crude preparation of ethylenebisquinol, which is insoluble in caustic soda, melts at 238°.

Ethylenecatechol, $C_6H_4<\begin{matrix}O{\cdot}CH_2\\ |\\ O{\cdot}CH_2\end{matrix}$, is prepared similarly to the foregoing compound; it is a colourless oil which boils at 124° (25 mm.), and distils under ordinary pressure at 216°. The *mononitro*-derivative melts at 121°. M. O. F.

Chlorinated Succinic acids and Chloromaleïc acid. By B. DE S. J. VAN DER RIET (*Annalen*, 1894, **280**, 216—232).—Isodichlorosuccinic anhydride is obtained by exposing to sunlight a solution of maleïc anhydride in liquid chlorine contained in a sealed tube; the corresponding acid melts at 170° (compare Michael and Tissot, Abstr., 1893, i, 143). The *dimethylic* and *diethylic* salts of isodichlorosuccinic acid are colourless oils, from which hydrogen chloride is eliminated spontaneously or by the application of heat. The *ammonium* salt contains $2H_2O$, the *calcium* and *copper* salts crystallise with $2\frac{1}{2}H_2O$, and the *lead* salt with $3H_2O$; the *barium* and *strontium* salts contain $7H_2O$.

When isodichlorosuccinic anhydride is heated in a reflux apparatus until the evolution of hydrogen chloride ceases, an almost quantitative yield of chloromaleïc anhydride is obtained, boiling at 194°. Treatment of this substance with water gives rise to the chloromaleïc acid obtained from trichloracetyl-β-chloracrylic acid (compare Zincke, Abstr., 1893, i, 318); the *strontium* salt forms silvery crusts containing $4\frac{1}{2}H_2O$.

Elimination of hydrogen chloride from dichlorosuccinic acid by means of hot aqueous sodium acetate yields chloromaleïc acid as the sole product, and the conclusion of Michael and Tissot (*loc. cit.*) that chlorofumaric acid is formed must therefore be attributed to the transformation of chloromaleïc acid into this substance under the influence of caustic alkali, this hydrolytic agent having been employed by the investigators named.

Trichlorosuccinic acid is formed when a mixture of 20 grams of chloromaleïc acid with 10 c.c. of water and 30 grams of liquid chlorine is exposed to sunlight for several hours in a sealed tube. The acid forms a colourless, highly-deliquescent crystalline mass, which gives no precipitate with silver nitrate; the metallic salts do not crystallise well. The *aniline* salt, $(NH_2Ph)_2C_4H_3Cl_3O_4$, melts at 146°; the *orthotoluidine* salt contains 1 mol. of alcohol, and decomposes before it melts. M. O. F.

Ethylic Amidoethylenedicarboxylate. By S. Ruhemann and R. S. Morrell (*Ber.*, 1894, **27**, 2743—2747).—Ethylic dicarboxyglutaconate reacts with aniline in the same way as with ammonia, *ethylic anilidoethylenedicarboxylate*, $NHPh{\cdot}CH{:}C(COOEt)_2$, being obtained together with ethylic malonate. The anilido-compound forms colourless crystals melting at 48—49°. Ethylic amidoethylenedicarboxylate is converted by ammonia into a monamide (Trans., 1892, 791), and reacts in a similar manner with aniline, ammonia being evolved and the *monanilide* of *ethylic anilidoethylenedicarboxylate*,

$$NHPh{\cdot}CH{:}C(CO{\cdot}NHPh){\cdot}COOEt,$$

formed; this substance crystallises in yellowish needles, and melts at 118°. A small amount of the monanilide is further decomposed, malondianilide and diphenylformamidine being produced. Similar results have been independently obtained by Band (*Inaug. Dissert.*, *Leipzig*, 1894).

Ethylic amidoethylenedicarboxylate is converted by hydrazine into ethylic isopyrazolonecarboxylate, $COOEt{\cdot}C\begin{matrix}CH{\cdot}NH\\ \diagup\\ CO{\cdot}NH\end{matrix}$, whilst with phenylhydrazine, it yields ethylic phenylisopyrazolonecarboxylate. A. H.

Disubstituted Succinic acids. By H. Kirchhoff (*Annalen*, 1894, **280**, 207—215).—Maleïc anhydride unites with bromine at ordinary temperatures, isodibromosuccinic acid being formed; the *calcium* salt has the constitution $C_4H_2Br_2O_4Ca + 3H_2O$. Dichlorosuccinic acid is prepared by exposing to sunlight fumaric acid in contact with liquid chlorine contained in a sealed tube (compare Michael and Tissot, Abstr., 1893, i, 142). The *silver* and *barium* salts are anhydrous, the *strontium* salt crystallises with $1H_2O$, the *calcium* salt with $2H_2O$, the *zinc*, *copper*, and *cadmium* salts with $3H_2O$. The *dimethylic* and *diethylic* salts melt respectively at 31·5—32° and 62°. M. O. F.

Synthetical Formation of Mesotartaric acid and Racemic acid. By F. Pollak (*Monatsh.*, 1894, **15**, 469—488).—In 1864, Schöyen prepared an acid by the action of alkalis on the additive product of glyoxal and hydrocyanic acid; he was unable to obtain it in a crystalline form, but, from the properties of its salts, it appeared to be a new isomeride of tartaric acid, and was, therefore, termed glycotartaric acid. Four years later, Strecker examined the products of the action of hydrochloric acid on the same additive compound, and obtained racemic acid, which he found to be quite different from Schöyen's acid. Since this time, no further investigation has been made, and the author has, therefore, taken the matter up again, and has succeeded in isolating the additive product of glyoxal and hydrocyanic acid, and also, to a large extent, in explaining the different results obtained by Schöyen and Strecker.

To prepare the cyanhydrin from glyoxal, it is necessary to avoid the presence of water, as decomposition then readily takes place: the most favourable results are obtained by heating an alcoholic solution of glyoxal with a 5 per cent. excess of alcoholic hydrogen cyanide at 80—90°, distilling off the alcohol in a vacuum, and allowing the syrupy residue to remain for some hours, when it solidifies to a magma of crystals. This, when treated with absolute ether, leaves a brownish, resinous mass, from which no definite substance could be obtained; the filtrate, on evaporation, yields a crystalline substance, which, after separating from the syrupy mother liquor and recrystallising, forms monosymmetric tablets, $a : b : c = 0{\cdot}8627 : 1 : 1{\cdot}4782$, $\epsilon = 90°\ 49{\cdot}5'$, and melts and is entirely decomposed at 131°; the analysis and molecular weight determination agree with the constitutional formula CN·CH(OH)·CH(OH)·CN. With benzoic chloride and alkali, it yields a *dibenzoyl* derivative melting at 67—69°, and, on heating with acetic anhydride at 60°, it is converted into the *diacetyl* derivative, CN·CH(OAc)·CH(OAc)·CN, which crystallises in lustrous, rhombic tablets, $a : b : c = 0{\cdot}7150 : 1 : 0{\cdot}6809$, melts at 75—77° (corr.), is readily soluble in the common solvents, and is optically inactive.

When treated with hydrochloric acid, it is converted into mesotartaric acid, which was identified by its physical properties and those of its calcium salt; the yield is very good, and no trace of any isomeride could be detected in the products of the action. The nitrile must, therefore, be regarded as *mesotartaric nitrile*. Strecker's inability to find this acid among the products of the action of hydrochloric acid on the crude nitrile is probably due to the fact that he extracted his calcium salts with an acetic acid solution, in which freshly prepared calcium mesotartrate is soluble.

The mother liquor from the mesotartaric nitrile does not deposit any more crystals, even after many weeks, but if it is heated with acetic anhydride at 60°, the product dissolved in ether, filtered, and the solution evaporated, a syrupy residue is left which after a time deposits crystals; by fractional crystallisation from ether, these may be separated into two crystalline compounds, one of which is diacetylmesotartaric nitrile, and the other an isomeric acetyl derivative, which crystallises in monosymmetric plates or prisms, $a : b : c =$

1·2569 : 1 : 2·6102, *ac* = 97° 15′, and melts at 97—98° (corr.). It is converted by the action of hydrochloric acid into racemic acid, and must, therefore, be *diacetylracemic nitrile*. The racemic acid thus prepared agrees in all its properties with the natural acid.

It appears probable that the racemic nitrile is not formed by the direct action of hydrogen cyanide on glyoxal, as the mother liquor from the mesotartaric nitrile does not yield it, if it is worked up at once, and the racemic derivative is therefore probably formed from the impure mesotartaric nitrile on long-continued standing. It is not formed by the action of acetic anhydride, as all attempts to bring about the change of the diacetylmesotartaric nitrile into the isomeride under similar conditions were without success.

Schöyen's glycotartaric acid was, in all probability, a mixture of mesotartaric acid with glycollic acid, the latter being formed by the action of alkalis on unaltered glyoxal still present. H. G. C.

Synthesis of Comenic acid: Chloropyromeconic acid. By A. Peratoner and R. Leone (*Gazzetta*, 1894, **24**, ii, 75—85).—Pyromeconic acid is readily prepared by subliming meconic acid at 260—310° in a current of carbonic anhydride, and treating the product with chloroform, in which it is very soluble; the comenic and meconic acids remain undissolved. Pyromeconic acid, when purified by resublimation, melts at 117°, but at 119—120° when contaminated with traces of comenic acid. Cryoscopic determinations in acetic acid solution show that pyromeconic acid has a molecular weight corresponding with the formula $C_5H_4O_3$.

Pure sodium pyromeconate, $C_5H_3O_3Na$, separates on treating a benzene solution of the acid with sodium. On heating it at 196° with carbonic anhydride under pressure, it is partly converted into sodium comenate. Comenic acid is therefore a carboxyl-derivative of pyromeconic acid.

Monochloropyromeconic acid, $C_5H_3ClO_3$, is obtained on treating pyromeconic acid with sulphuryl chloride; it crystallises in long, colourless, flattened needles, which melt at 181° and sublime at the ordinary temperature. It does not decompose alkali carbonates, and is very soluble in organic solvents or water.

Meconic and comenic acids do not react with sulphuryl chloride.

W. J. P.

Furfurylic and other Nitrites. By G. Bertoni (*Gazzetta*, 1894, **24**, ii, 20—25).—*Furfurylic nitrite*, $C_4OH_3{\cdot}CH_2{\cdot}ONO$, may be readily prepared by gradually adding trinitroglycerol to furfurylic alcohol cooled by a freezing mixture. It separates as a heavy, yellowish oil possessing a not unpleasant odour; in a few days it turns brown and resinifies. It is soluble in ether, chloroform, or glycerol, but is insoluble in water; the acetic acid solution soon decomposes. Potash, mineral acids, and methylic or ethylic alcohol immediately decompose the nitrite; hydrogen sulphide and ammonium sulphide act on it with separation of sulphur. Furfurylic nitrite has a sp. gr. of 1·165 at 11°; it remains unchanged at 100°, but at 126—127° it begins to boil violently and decomposes, leaving an

abundant carbonaceous residue. The following nitrites were prepared by processes similar to the above.

Isobutyleneglycollic nitrite, $NO{\cdot}O{\cdot}CMe_2{\cdot}CH_2{\cdot}O{\cdot}NO$, is very sensitive to light and is decomposed by water or acids. It has a sharp taste, boils and decomposes at 128° with evolution of red vapours, and has a sp. gr. of 1·092 at 0°. Methylic alcohol reconverts it into the glycol.

Ethylenic acetonitrite, $CH_3{\cdot}COO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO$, gives off nitrous oxide when in contact with water, has a pleasant ethereal odour, and boils at 130°.

Ethylenechlorhydrin nitrite, $CH_2Cl{\cdot}CH_2{\cdot}O{\cdot}NO$, has an unpleasant, penetrating odour, and continually evolves chlorine and nitrous oxide; at 117° it boils and decomposes.

Dichlorhydrin nitrite, $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}NO$, resembles the preceding nitrite, and is converted into the dichlorhydrin by methylic alcohol; it boils and decomposes at 155—160°.

Chloral nitrite, $CCl_3{\cdot}CH(O{\cdot}NO)_2$, is a heavy, unstable oil, which begins to boil at 70°, and is totally decomposed at 75°.

Cetylic nitrite, $C_{16}H_{13}{\cdot}O{\cdot}NO$, is fairly stable, and melts at about 20°; it decomposes at 190—200°, evolving nitric oxide in abundance.

W. J. P.

αα-Dithienyl. By O. Eberhard (*Ber.*, 1894, **27**, 2919).—αα-Dithienyl may be obtained by heating α-iodothiophen with silver, prepared by means of an alkaline solution of glucose, and is identical with the dithienyl obtained by Töhl. On oxidation with a boiling solution of potassium permanganate, it is converted into α-thiophenic acid.

Dithienyl is not formed when α-bromo- or α-iodo-thiophen is treated with sodium in presence of ether or when the iodo-derivative is heated with zinc-dust or with silver reduced by means of ferrous sulphate.

A. H.

Preparation of Phenylnitromethane. By S. Gabriel (*Ber.*, 1894, **27**, 2738).—In view of the criticism of Werner and Buss (*Ber.*, **27**, 2193), the author has had the method of preparation of phenylnitromethane, which has been already described by him (*Ber.*, **18**, 1251), carried out afresh, and finds that it is perfectly satisfactory.

A. H.

Ethereal Salts of Catechol with Phosphorous and Sulphurous Acids. By R. Anschütz and W. Posth (*Ber.*, 1894, **27**, 2751—2753).—*Catechol phosphite*, $P_2(O_2{\cdot}C_6H_4)_3$, is formed when catechol is heated in benzene solution with phosphorus trichloride. It is a colourless liquid, boils at 202—203° under a pressure of 1 mm., and, on exposure to air, rapidly changes into a solid substance melting at 100—101°; this has not yet been further investigated.

Catechol sulphite, $C_6H_4{<}\overset{O}{\underset{O}{>}}SO$, is obtained in a similar manner from catechol and thionyl chloride. It is a colourless, mobile liquid, boils at 210—211°, and has a sp. gr. = 1·409 at 15°. Its vapour has an unpleasant odour, and causes a flow of tears.

A. H.

Action of Phosphorus Pentachloride on Tetrachloroquinone. By E. Barral (*Compt. rend.*, 1894, **119**, 280—281).—When quinone (1 mol.) and phosphorus pentachloride (2 mols.) are heated together at 130—140° for many hours, they yield a yellow liquid, which, on cooling, solidifies to a white solid. The action is accelerated by the presence of a small quantity of phosphorus trichloride. The product is thrown into water, washed, dried, and heated with hot benzene, which leaves an abundant residue, probably consisting of pentachlorophenol phosphate. The benzene solution, when very slowly evaporated, yields a mixture of long needles of hexachlorobenzene and large prisms of hexachlorobenzene dichloride, impregnated with oily matter which has the odour of chloroquinone. The hexachlorobenzene dichloride melts at 159—160°, and is identical with that previously described (Abstr., 1894, i, 406). It crystallises from light petroleum in long prisms, and from benzene in large, monoclinic prisms. It sublimes without change at a temperature below 200°, but if more strongly heated decomposes into hexachlorobenzene and chlorine. In presence of phosphorus pentachloride, decomposition takes place at a temperature much below 200°, and this probably explains why Graebe obtained hexachlorobenzene only on heating tetrachloroquinone with phosphorus pentachloride at 180°. Fuming nitric acid oxidises hexachlorobenzene dichloride to tetrachloroquinone. It would follow that quinone is a true diketone. C. H. B.

Diisosafrole and Cubebin. By A. Angeli and P. Mole (*Gazzetta*, 1894, **24**, ii, 127—130).—*Diisosafrole* ($C_{10}H_{10}O_2)_2$, is prepared by heating isosafrole with a saturated alcoholic solution of hydrogen chloride at 160° in closed tubes. It crystallises in thin, white needles sparingly soluble in cold alcohol; it melts at 145°, and is found, by cryoscopic determinations, to have the molecular composition indicated above.

The authors were unable to prepare Weidel's tribromocubebin (*Jahresb.*, 1877, 931), but obtained *dibromocubebin*, $C_{10}H_8Br_2O_2$, by direct bromination of cubebin. The new derivative forms small, white crystals melting at 229°.

Isosafrole and cubebin are undoubtedly very nearly related, and the authors have undertaken their investigation with the object of throwing some light on the constitution of cubebin. W. J. P.

Sulphur in Aniline and Paramidophenol, and the Calcium Hypochlorite Reaction. By A. Hantzsch and H. Freese (*Ber.*, 1894, **27**, 2966—2968).—The aniline employed was prepared from benzene which had been purified with sulphuric acid: it was boiled for 10 hours with 10 per cent. of acetone; the quantity of sulphur found varied from 0·0027—0·0041 per cent. Further experiments show that aniline, from the most varied sources and of undoubted purity, gives the calcium hypochlorite reaction (compare Abstr., 1894, i, 572); nitro-, dinitro-, and amido-thiophen do not. So far, the previous conclusions must be amended; but there appears to be a connection between the browning of aniline and the sulphur which it contains. J. B. T.

Oxidation of Aromatic Orthodiamines and Orthamidophenols. By O. FISCHER and O. JONAS (*Ber.*, 1894, **27**, 2782—2785).—The oxidation product of orthoamidoditolylamine previously described by Fischer and Sieder (Abstr., 1891, 434), has been again analysed, and its molecular weight determined, it appears to be an indone, $C_6H_3Me^{6}\!<\!\!\begin{array}{c}\text{———}\\ N(C_7H_7)^{3}\end{array}\!\!>\!\!\overset{2}{N}\!>C_6\overset{2}{H}Me\overset{1}{O}\cdot\overset{3}{N}H\overset{4}{C}_7H_7$. The corresponding induline could not be isolated. By the action of alcoholic potash, the indone is converted into an isomeric compound which is probably a fluorindine- or triphendioxazine-derivative

$$C_6H_3Me\!<\!\!\begin{array}{c}\text{—NH—}\\ N(C_7H_7)\end{array}\!\!>\!C_6HMe\!<\!\!\begin{array}{c}\overset{6}{\text{—O—}}\\ \underset{5}{NH}\end{array}\!\!>\!C_6H_3\overset{2}{Me}\,;$$

it crystallises in red needles, melts at 260°, is a strong base, and gives a violet coloration with sulphuric acid.

Orthamidophenol, when oxidised with mercuric oxide, yields the compound $C_6H_4\!<\!\overset{2}{N}\!\!>\!\!\begin{array}{c}\\ O^{3}\end{array}\!\!>\!C_6\overset{1,4}{H}_2\overset{3}{O}\cdot\overset{2}{N}H_2$, the analogue of diamidophenazine; this crystallises in small, dark red crystals, melts at 249°, is insoluble in alkalis, and, with sulphuric acid, gives a violet coloration, changing to red on dilution. The *hydrochloride* crystallises in dark brown needles; the *platinochloride* forms deep red, lustrous crystals: both are sparingly soluble; the *aurochloride* crystallises in bronze-coloured, lustrous needles.

It is characteristic of the benzeneorthodiamines and orthamidophenols that on oxidation 2 mols. combine to form phenazine- and phenoxazine-derivatives, whilst the corresponding naphthalene compounds yield quinones; this is probably the reason of the difficulty which is experienced in preparing benzeneorthoquinones by methods similar to those which readily yield 1-2-naphthaquinones.

J. B. T.

Stereoisomeric Potassium Benzenediazosulphonates. By E. BAMBERGER (*Ber.*, **27**, 2930—2939; compare *Ber.*, 1894, **27**, 2586).—The author criticises in detail the arguments put forward by Hantzsch (Abstr., 1894, i, 597) in support of his view, that the orange and yellow salts obtained by the action of potassium sulphite on diazobenzene salts are stereoisomeric. The orange salt has all the properties of a sulphite, evolves sulphurous anhydride when treated with dilute acids, decolorises iodine and potassium permanganate solutions, and reduces cupric thiocyanate. Attempts to repeat the analysis of the salt show that trustworthy numbers cannot be obtained owing to the rapid decomposition and molecular change which occur. The author considers that all the properties of the orange salt indicate that it is a complex diazobenzene sulphite, the spontaneous change of which into a sulphonate would be quite in accordance with our knowledge of the relations between the sulphites and sulphonates of the fatty series.

A. H.

Formation of Dyes from Stereoisomeric Diazo-compounds, and the Configuration of Diazo-ethers. By A. HANTZSCH (*Ber.*, 1894, **27**, 2968—2975).—A polemical reply to Bamberger's criticisms (Abstr., 1894, i, 580) of the author's recent communications on stereoisomeric diazo-compounds. It is admitted that the author was in error in considering the diazoamido-compounds and bisdiazoamido-compounds as stereoisomeric; the difference in composition is small, and the latter compounds are readily, often spontaneously, converted into the former. Potassium nitroantidiazobenzene reacts in the course of a few seconds with sodium β-naphthol containing a little free alkali; the action is slower the larger the quantity of free alkali present. Potassium benzeneantidiazosulphonate, the yellow stable salt, reacts in a similar manner, but more slowly. Anti(iso)-diazo-derivatives, therefore, as such, combine with alkali phenols, but less rapidly than the syn-derivatives: the difference is merely one of degree, as is usually the case with stereoisomeric compounds. Nitrodiazobenzene methyl ether closely resembles sodium nitrodiazobenzene in its action on naphthol, but with alkali in excess the solution becomes instantaneously violet; this difference is not due to hydrolysis of the ether, but arises from the fact that the alkali, although without direct action on the ether, exerts considerable influence on solutions of the sodium salt or on diazo-derivatives with acidic properties. The violet colour is caused by the formation of a sodium salt which is much more readily soluble than the red dye itself, and is, therefore, more easily formed. The direct proof that the ether is an "anti"-derivative can only be afforded by the preparation of the "syn"-compound; but it is unlikely that this can exist, as, in addition to the characteristic instability of "syn"-derivatives, it would be hydrolysed with the greatest ease. J. B. T.

Reduction Products of Azo-compounds. By P. JACOBSON and P. PIEPENBRINK (*Ber.*, 1894, **27**, 2700—2714.).—When metatolueneazo-paracresetoïl, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}OEt$ [N : Me : OEt = 1 : 3 : 6], is reduced with stannous chloride and hydrochloric acid, it undergoes the benzidine transformation, yielding a diphenyl-derivative, dimethylethoxydiamidodiphenyl, $NH_2{\cdot}C_6H_3Me{\cdot}C_6H_2Me(NH_2){\cdot}OEt$ [$Me_2 : (NH_2)_2 : OEt = 2 : 2' : 4 : 4' : 5$]. But when paratolueneazoparacresetoïl, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}OEt$, in which the Me of the C_6H_4Me-group occupies the para-position, is reduced, a benzidine transformation is no longer to be expected, and, in fact, a diphenyl-derivative (boiling at 237—243° under 35 mm. pressure, and yielding a yellow orthohydroxybenzylidene-derivative which melts at 106°) is only formed in small amount; the main action is a semidine transformation, with formation of a diphenylamine-derivative, dimethylethoxyamidodiphenylamine,

$C_6H_4Me{\cdot}NH{\cdot}C_6H_2Me(NH_2){\cdot}OEt$ [NH : Me : NH_2 : OEt = 1 : 2 : 4 : 5]; but at the same time some of the azo-compound is decomposed, with formation of paratoluidine and a cresetidine, [NH_2 : Me : OEt = 1 : 3 : 6].

Metatolueneazoparacresol, prepared by diazotising metatoluidine and treating the product with paracresol, is a brown substance melting at 95°. When boiled with sodium ethoxide and ethylic bromide in

alcoholic solution, it yields the *cresetoïl*, which melts at 76°. *Dimethylethoxydiamidodiphenyl* yields a *dihydrochloride* and a yellow *di-orthohydroxybenzylidene*-derivative melting at 127°.

Paratolueneazoparacresetoïl melts at 43°; not at 171°, as Noelting and Werner state (Abstr., 1891, 214). *Dimethylethoxyamidodiphenylamine* melts at 108—109°; with acetic acid, it yields a *monacetyl*-derivative melting at 125°; with carbon bisulphide, a *thiocarbamide* melting at 167·5°. The *orthohydroxybenzylidene* derivative melts at 157°. With acetic chloride, it yields a *diacetyl* derivative melting at 165°; and, when oxidised with chromic acid, a red *ethoxytoluquinonetoluidide*, $C_6H_4Me{\cdot}N{:}C_6H_2MeO{\cdot}OEt$, is found melting at 76°. The latter yields paratoluidine when hydrolysed; the other product, presumably ethoxytoluquinone, could not be isolated. C. F. B.

Derivatives of 2 : 4-Dinitrophenylhydrazine and Picrylhydrazine; Action of Hydrazine Hydrate on Chloranil. By A. Purgotti (*Gazzetta*, 1894, **24**, i, 554—584; compare Abstr., 1894, i, 372, and next abstract).—2 : 4 *Dinitrophenylhydrazine*, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH_2$, is prepared by boiling an alcoholic solution of 1 : 2 : 4-metadinitrochlorobenzene and hydrazine hydrate; it forms transparent yellow crystals having a red fluorescence, or small pleochromatic prisms melting at 194°. It dissolves sparingly in the usual solvents, and is decomposed by soda with formation of 1 : 2 : 4-metadinitrophenol. The *hydrochloride* crystallises in yellow, pleochromatic needles which lose hydrogen chloride at 110°, leaving the base; it melts at 150° in a closed tube.

Acetyl-2 : 4-*dinitrophenylhydrazine*, $C_6H_3(NO_2)_2{\cdot}N_2H_2Ac$, obtained by heating the base with acetic acid, crystallises in thin, yellow pleochromatic needles melting at 193—194°.

Oxaldinitrodiphenylhydrazine, $C_2O_2[N_2H_2{\cdot}C_6H_3(NO_2)_2]_2$, is prepared by heating a mixture of ethylic oxalate with the dinitrophenylhydrazine. It forms yellow crystals which darken at 270°, and melt at 292°.

2 : 4-*Dinitrodiphenylthiosemicarbazide*, $NHPh{\cdot}CS{:}N_2H_2{\cdot}C_6H_3(NO_2)_2$, prepared by boiling the base with phenylthiocarbimide in alcoholic solution, forms yellow, lustrous, tabular crystals melting at 186°; it is decomposed by soda, and by boiling water. The hydrazine is converted into 2 : 4-dinitrophenylazoimide, $\begin{matrix}N\\ \|\\ N\end{matrix}\!>\!N{\cdot}C_6H_3(NO_2)_2$, by dissolving it in sulphuric acid, and treating it with sodium nitrite.

2 : 4-*Dinitrophenylhydrazomethane*, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}N{:}CH_2$, separates on mixing formaldehyde with the hydrazine dissolved in dilute sulphuric acid; it separates from its alcoholic solution in tiny yellow crystals melting at 155°. The corresponding *ethane* derivative is obtained from acetaldehyde, and crystallises in yellow scales melting at 147°. The *benzylidene* derivative, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}N{:}CHPh$, prepared from benzaldehyde, crystallises in microscopic yellow needles and melts at 203°. The *orthohydroxybenzylidene* derivative, $C_6H_3(NO_2)_2{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}OH$, prepared from salicylaldehyde, crystallises in minute yellow needles melting at 237°; its *para*-isomeride is amorphous and melts at 157°. The *orthonitrobenzylidene* derivative

is obtained from orthonitrobenzaldehyde and melts at about 192°; its *meta*-isomeride melts at 268°.

Cinnamylidene-2 : 4-*dinitrophenylhydrazine*,

$$C_6H_3(NO_2)_2\cdot N_2H{:}CH\cdot CH{:}CHPh,$$

prepared from cinnamaldehyde, crystallises in small, bright red scales.

Furfurylidenedinitrophenylhydrazine, $C_6H_3(NO_2)_2\cdot N_2H{:}CH\cdot C_4H_2O$, is obtained from furfuraldehyde, and crystallises in scarlet laminæ melting at 202°.

Dinitrophenylhydrazopropane, $C_6H_3(NO_2)_2\cdot N_2H{:}CMe_2$, crystallises in minute, yellow tablets melting at 118°.

Ethylic dinitrophenylhydrazoacetoacetate,

$$C_6H_3(NO_2)_2\cdot N_2H{:}CMe\cdot CH_2\cdot COOEt,$$

is obtained by the action of ethylic acetoacetate on the hydrazine; it crystallises in thin, yellow needles melting at 95°.

Dinitrophenylhydrazobenzophenone, $C_6H_3(NO_2)_2\cdot N_2H{:}CPh_2$, obtained from benzophenone, forms small, orange-yellow needles melting at 229°.

Dinitrophenylhydrazobenzile, $C_6H_3(NO_2)_2\cdot N_2H{:}CPh\cdot COPh$, is obtained from benzile, and crystallises in very minute orange-yellow laminæ melting at 183—184°.

Acetylpicrylhydrazine, $C_6H_2(NO_2)_3\cdot N_2H_2Ac$, is prepared by boiling an acetic acid solution of picrylhydrazine; it crystallises in very thin, yellow needles melting at 210°.

Oxaldipicrylhydrazine, $C_2O_2[N_2H_2\cdot C_6H_2(NO_2)_3]_2$, prepared from ethylic oxalate and picrylhydrazine, crystallises in yellowish needles melting at 175°.

Picrylazoimide, $C_6H_2(NO_2)_3\cdot N_3$, crystallises in thin, yellow needles melting at 70°.

Ethylidenepicrylhydrazine, $C_6H_2(NO_2)_3\cdot N_2H{:}CHMe$, is obtained in red laminæ melting at 119—120°.

Benzylidenepicrylhydrazine, $C_6H_2(NO_2)_3\cdot N_2H{:}CHPh$, is obtained in thin, yellow needles melting and decomposing at 248°. *Orthonitrobenzylidenepicrylhydrazine* and its *meta*-isomeride form small, yellow crystals melting at 215° and 250—251° respectively.

Orthohydroxybenzilidenepicrylhydrazine,

$$C_6H_2(NO_2)_3\cdot N_2H{:}CH\cdot C_6H_4\cdot OH,$$

and its *para*-isomeride are obtained as crystalline powders melting and decomposing at 275° and 284° respectively.

Cinnamylidenepicrylhydrazine is obtained in small, red crystals melting at 200°. *Furfurylidenepicrylhydrazine* forms small, yellow crystals having a red fluorescence and melting at 230°.

Picrylhydrazopropane and the *picrylhydrazone* of ethylic acetoacetate crystallise in yellow needles melting at 125° and 165° respectively.

Chloranil dissolves in a warm alcoholic solution of hydrazine hydrate with evolution of nitrogen and formation of a *compound* of hydrazine and tetrachloroquinol, $C_6Cl_4(OH)_2,2N_2H_4$; it crystallises in small needles melting at 183°. W. J. P.

Synthesis of Aromatic Hydrazines from Hydrazine Hydrate. By T. CURTIUS and G. M. DEDICHEN (*J. pr. Chem.*, 1894, [2], **50**, 241—274; compare preceding abstract).—Hydrazine hydrate does not yield aromatic hydrazines when heated, in presence of caustic baryta, with iodobenzene, paranitraniline, paraiodo- or parabromo-nitrobenzene, or the para-halogen substitution derivatives of aniline.

On the other hand, it reacts in the cold with 1 : 2 : 4-chloro- or bromo-dinitrobenzene to form 2 : 4-*dinitrophenylhydrazine*,

$$C_6H_3(NO_2)_2\cdot NH\cdot NH_2,$$

which crystallises from alcohol in splendid, deep violet, flat prisms, melting and decomposing at 198°. It is very sparingly soluble in cold alcohol, insoluble in water and cold acids, readily soluble in alkalis, and reduces Fehling's solution and ammoniacal silver oxide solution. It is very stable towards acids, and may be recrystallised from glacial acetic acid. The *hydrochloride* crystallises in yellow, lustrous plates, which are decomposed by water and alcohol, the free base being formed; the whole of the acid is lost at 150°. The *nitrate* forms small, hard, nacreous plates, and, like the hydrochloride, is decomposed by water and alcohol, but melts at 158—160° without decomposing.

The hydrazine dissolves readily in alkalis, forming deep red solutions, which decompose on boiling, dinitrophenol being formed and ammonia evolved. The *sodium* salt probably has the formula $C_6H_3(NO_2)_2\cdot NNa\cdot NH_2$, and is an amorphous, reddish-yellow mass, which decomposes very readily and explodes when heated. Dinitrophenylhydrazine does not appear to combine directly with carbon bisulphide. *Acetyldinitrophenylhydrazine*, $C_6H_3(NO_2)_2\cdot NH\cdot NHAc$, is obtained by the action of acetic anhydride on the base, and crystallises in slender, pale yellow, silky needles, melting at 197—198°; alkalis give with it a red coloration, which changes to light yellow on the addition of an acid.

Dinitrophenylnitrosohydrazine, $C_6H_3(NO_2)_2\cdot N(NO)\cdot NH_2$, is obtained as an oil, which solidifies to a crystalline mass; it melts at 72°, and deflagrates when heated in a test-tube. It decomposes when kept, and is also partially decomposed by boiling alcohol, but may be recrystallised from ether, from which it separates in large, thick prisms; these, however, soon fall to a yellow powder.

Dinitrophenylazoimide, $C_6H_3(NO_2)_2\cdot N_3$, is formed when the nitroso-compound is boiled with water or allowed to stand in a desiccator, and is a pale yellow powder, melting at 56°. It is decomposed into dinitrophenol and azoimide when boiled with an alkali.

Dinitrophenylhydrazine readily reacts in the characteristic manner with aldehydes and ketones. *Benzylidenedinitrophenylhydrazine*,

$$C_6H_3(NO_2)_2\cdot NH\cdot N{:}CHPh,$$

forms orange-coloured plates, melting at 235°. *Orthohydroxybenzylidenedinitrophenylhydrazine* crystallises from alcohol in purple-red, slender, matted needles, melting at 248°. *Acetonedinitrophenylhydrazone* forms slender, yellow needles, and melts at 128°. Ethylic acetoacetate also reacts with the hydrazine, forming a *condensation product*,

$C_6H_3(NO_2)_2 \cdot NH \cdot N{:}CMe \cdot CH_2 \cdot COOEt$,

which crystallises from dilute alcohol in deep, orange-yellow prisms, melting at 96°. These compounds are, as a rule, readily decomposed by alkalis, with difficulty by acids.

In order to definitely establish the identity of the derivatives of phenylhydrazine with those prepared directly from hydrazine hydrate, dinitraniline was converted into dinitrophenylhydrazine by means of the diazo-reaction, and was found to be identical in every respect with the synthetical product.

2 : 4-*Dinitrodiazobenzene nitrate* forms lustrous, yellowish plates, which explode violently when heated in a test-tube. It reacts with resorcinol to form a colouring matter, *dinitrobenzeneazoresorcinol*, which is a microcrystalline, dark reddish-brown powder, with a green lustre, and dyes wool and silk a golden-brown.

Picrylic chloride reacts violently with hydrazine hydrate to form *picrylhydrazine* (1 : 2 : 4 : 6-*trinitrophenylhydrazine*),

$C_6H_2(NO_2)_3 \cdot NH \cdot NH_2$,

which crystallises in small, hard prisms of a deep, reddish-brown colour. It melts at 186°, and explodes feebly when heated in a tube. It is almost insoluble in benzene, sparingly soluble in cold alcohol, readily in acetic acid. It has a more acid character than the dinitro-compound, does not form salts with acids, and is more readily attacked by alkalis, forming blue solutions. It reduces both Fehling's solution and ammoniacal solutions of silver oxide. *Acetylpicrylhydrazine* crystallises in greenish-yellow prisms with a silky lustre, and melts at 223°.

Benzylidenepicrylhydrazine crystallises in orange-coloured, matted needles, and melts at 267°. It is insoluble in water and dilute acids, and is decomposed by dilute alkalis. *Acetonepicrylhydrazone* forms slender, brown needles, melting and decomposing at 125°.

Hydrazine hydrate reacts with paranitrophenylazoimide in a remarkable manner, paranitraniline and a little nitrobenzene being formed, along with nitrogen and ammonia, the chief action occurring according to the equation $3NO_2 \cdot C_6H_4 \cdot N_3 + 3N_2H_4,H_2O = 3NO_2 \cdot C_6H_4 \cdot NH_2 + 5N_2 + 2NH_3 + 3H_2O$. A similar action takes place between hydrazine hydrate and phenylazoimide, aniline and traces of benzene being formed, in addition to ammonia and nitrogen. Benzoylazoimide, on the other hand, is converted into benzoylhydrazine, azoimide being liberated.

Hydrazine hydrate combines directly with cyanogen to form *carbohydrazimine*, $NH_2 \cdot NH \cdot C(NH) \cdot C(NH) \cdot NH \cdot NH_2$, which crystallises from dilute alcohol in flat, colourless needles. It is readily soluble in water, and, when heated, decomposes gradually without melting.

This substance contains two hydrazine residues, and therefore reacts with aldehydes and ketones.

Benzylidenecarbohydrazimine, $C_2(NH)_2(NH \cdot N{:}CHPh)_2$, is formed by the direct condensation of carbohydrazimine with benzaldehyde. It crystallises in light, bronze-coloured plates, and melts at 218°.

Acetonitrile does not react with hydrazine hydrate in the cold, but at 150° *methylhydrazicarbimine*, $NH{:}CMe \cdot NH \cdot NH \cdot CMe{:}NH$, is formed.

It is readily soluble in alcohol, and melts at 197—198°. It does not form condensation products with aldehydes, and does not yield hydrazine when boiled with dilute acids or alkalis, but is decomposed by concentrated potash with evolution of ammonia.

Phenylhydrazicarbimine is obtained from hydrazine hydrate and benzonitrile in a similar manner. It forms colourless, lustrous plates, melts at 250°, and is insoluble in water, dilute acids, and alkalis. Paratolunitrile does not react with hydrazine hydrate under the same conditions. A. H.

α-Acetylphenylhydrazine. By O. Widman (*Ber.*, 1894, **27**, 2964—2965).—All attempts to prepare α-acetylphenylhydrazine, by the author's method (Abstr., 1893, i, 411), from β-acetylphenylhydrazine, failed, but Pechmann and Runge's description of its properties (Abstr., 1894, i, 457) has indicated the necessary conditions, and it can be obtained by heating diacetylphenylhydrazine with 10 parts of dilute sulphuric acid (10 per cent.) for 30 minutes at 70—80°. The yield is about 10 per cent. of the diacetyl-derivative employed. α-Acidylphenylhydrazines are readily distinguished from β-acidyl and αβ-diacidyl derivatives, as the latter give Bülow's reaction and the former do not. J. B. T.

Orthamidobenzylhydrazines. By M. Busch (*Ber.*, 1894, **27**, 2897—2904; compare Abstr., 1892, 734).—*Orthonitrobenzylphenylnitrosamine*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NO$, is prepared by the action of sodium nitrite on orthonitrobenzylaniline, and crystallises from ether in well-developed, vitreous prisms, melting at 84°. When it is treated in ethereal solution with hydrogen chloride, it undergoes molecular change, and is converted into *orthonitrobenzylnitrosoaniline*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NO,$$

which forms steel-blue needles, melting at 165—167°. The reduction of the nitrosamine with tin and hydrochloric acid leads to the formation of phenylindazole, with sodium amalgam and alcohol, to orthamidobenzylaniline, and with zinc dust and acetic acid, to *orthamidobenzylphenylhydrazine*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NH_2$. The last of these crystallises in vitreous needles, melts at 102°, and is a powerful base. The *oxalate* crystallises in colourless needles, melting at 138°, whilst the salts with mineral acids are deliquescent. Phosgene reacts with the hydrazine base forming a *condensation product* of the formula

$$C_6H_4 < \begin{matrix} NH—CO \\ CH_2 \cdot NPh \end{matrix} > NH.$$

This substance separates from acetic acid in compact crystals, melting and decomposing at 281°. Carbon bisulphide reacts with the free base to form the corresponding *thio-derivative*, $C_6H_4 < \begin{matrix} NH—CS \\ CH_2 \cdot NPh \end{matrix} > NH$, which forms compact crystals, and melts and decomposes at 243°. The instability of the ring of seven atoms, which is present in this compound, is shown by the fact that, when the substance is reduced, ammonia is eliminated and phenyltetrahydroquinazoline produced.

Orthamidobenzylphenylhydrazine reacts with benzaldehyde to form a *dibenzylidene compound*, $CHPh{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPh{\cdot}N{:}CHPh$, which crystallises in yellow needles, and melts at 148—150°.

Similar derivatives have been obtained from *orthonitrobenzylparaphenetylnitrosamine*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(NO){\cdot}C_6H_4{\cdot}OEt$, which crystallises in orange-coloured plates and melts at 95°. *Orthamidobenzylphenetylhydrazine* forms colourless, rhomboidal tablets, and melts at 98°. The *oxalate* crystallises in slender, white needles. Carbon bisulphide and the base yield a *thiocarbamide* derivative,

$$NH<\begin{matrix}CS-NH\\C_6H_4{\cdot}CH_2\end{matrix}>N{\cdot}C_6H_4{\cdot}OEt,$$

which crystallises in lustrous needles and melts at 198°.

Dibenzylideneorthamidobenzylparaphenetylhydrazine crystallises in lemon-yellow prisms, and melts at 152°. A. H.

Hydrazides and Azides of Organic Acids. By T. Curtius (*J. pr. Chem.*, 1894, [2], **50**, 275—294).—The author applies the term *acid hydrazides* to substances of the formula $R{\cdot}CO{\cdot}NH{\cdot}NH_2$, whilst the derivatives of azoimide are designated by the term *acid azides*, and have the formula $R{\cdot}CO{\cdot}N_3$.

The acid hydrazides are formed by the action of hydrazine hydrate on the ethereal salts of the organic acids, and the acid amides, chlorides, and azides, whilst the sulphohydrazides may be obtained in a similar manner from the corresponding sulphochlorides. The ethereal salts of the bibasic acids act in the same manner, two hydrazine residues being introduced. The imides and anhydrides of these acids, on the other hand, only react with 1 mol. of hydrazine. The reactions all take place in the cold, some even with explosive violence. The compounds thus produced are crystalline, colourless substances, which have powerful reducing properties, and are soluble in dilute acids. They are stable towards acids and alkalis, although some of the hydrazides of the fatty acids are decomposed by these reagents, with formation of hydrazine and the acid. By the introduction of an acid radicle, the basic character of the hydrazine is weakened to a less extent than that of ammonia, the hydrazides being distinctly basic; they form crystalline and stable salts, which unite with the chlorides of gold and platinum to form double salts, the metallic compound being usually reduced to a lower state of oxidation. One of the hydrogen atoms of the hydrazine residue can be displaced by the alkali metals or by silver; the sodium derivatives are crystalline and hygroscopic. The acid hydrazides yield acetyl derivatives when treated with acetic chloride or anhydride, but the exact constitution of these compounds has not yet been ascertained. The primary hydrazides may also be obtained by the action of hydrazine hydrate on acid derivatives of ethylic glycollate, benzhydrazide having been, first of all, prepared in this way. The reaction is as follows:

$$OBz{\cdot}CH_2{\cdot}COOEt + 2N_2H_4{,}H_2O = OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + NHBz{\cdot}NH_2 + EtOH + 3H_2O$$

glycollic hydrazide being formed, and not hydrazineacetic acid, as

previously supposed. When glycollic hydrazide is heated with water, it is converted into hydraziglycollide, $CO<^{CH_2\cdot NH\cdot NH}_{NH\cdot NH\cdot CH_2}>CO$. Alkyl derivatives of ethylic glycollate behave towards hydrazine hydrate in the normal manner, the corresponding alkyl glycollic hydrazide being obtained.

All the primary hydrazides react with aldehydes and ketones to produce colourless condensation products, generally sparingly soluble.

The secondary symmetrical hydrazides are formed when hydrazine hydrate is acted on with an excess of an ethereal salt of an organic acid, or when the latter substance is added to a primary hydrazide. They are also produced by the oxidation of the primary hydrazides by means of iodine or mercuric oxide, and when the primary hydrazides are heated for some time above their melting points, hydrazine being eliminated, generally in the form of ammonia and nitrogen. The hydrazides of the bibasic acids behave in a similar manner, oxalhydrazide, $NH_2\cdot NH\cdot CO\cdot CO\cdot NH\cdot NH_2$, for example, yielding a dioxalhydrazide, which probably has the constitution $CO<^{CO\cdot NH\cdot NH}_{NH\cdot NH\cdot CO}>CO$. The secondary symmetrical hydrazides are colourless substances of high melting point, and have faintly basic properties. They are even more stable towards acids than the primary compounds, and do not react with aldehydes and ketones.

Action of Nitrous acid on Acid Hydrazides.—The primary acid hydrazides are usually converted into acid azides by the action of nitrous acid, nitroso-compounds being most probably formed as intermediate products. The hydrazides of the bibasic acids, with the exception of fumaric and carbonic acids, however, yield no acid azide, but are converted into substances which are identical with the products obtained by the action of oxidising agents on them. The acid azides may also be prepared by the action of nitric acid on the hydrazides, or by treating these with aqueous diazobenzene sulphate (Abstr., 1893, i, 463). Benzoylazoimide, $Bz\cdot N_3$, and the azides of the substituted benzoic acids, melt at low temperatures, and decompose more or less violently when heated considerably above their melting points. They are poisonous, have no decided acid or basic properties, and are converted by warming with acids or bases into azoimide and the corresponding acid. Reducing agents either decompose the azides into azoimide and the corresponding acid, which then undergoes secondary changes (alcoholic ammonium sulphide, alcohol and sodium amalgam), or convert them into nitrogen and the corresponding acid amide, $BzN_3 + H_2 = BzNH_2 + N_2$ (acid reducing agents), or act on two molecules, which unite to form a secondary hydrazine, two-thirds of the nitrogen being evolved in the form of gas, $2Bz\cdot N_3 + H_2 = Bz\cdot NH\cdot NH\cdot Bz + 2N_2$ (energetic reduction in alkaline solution).

The azides are completely decomposed if boiled with water for some time. Benzoylazoimide, for example, is thus quantitatively decomposed according to the equation $2BzN_3 + H_2O = 2N_2 + CO_2 + CO(NHPh)_2$. When boiled with alcohol, a similar change occurs, urethanes being formed (Abstr., 1894, i, 331). Similar changes are produced by bromine, which converts benzoylazoimide into

bromocarbanil and nitrogen, $BzN_3 + Br_2 = CO{:}NPhBr_2 + N_2$, and by hydrogen chloride in ethereal solution, hippurazide being thus converted into hippurocarbanil hydrochloride, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}N_3 + HCl = N_2 + NHBz{\cdot}CH_2{\cdot}N(CO)HCl$. The compound previously described as diazohippuramide is actually hippurazide,

$$NHBz{\cdot}CH_2(CO){\cdot}N_3.$$

Aniline, in ethereal solution, decomposes the acid azides, with liberation of azoimide and formation of the anilide of the organic acid, whilst an excess of aniline, when heated with benzazide, yields diphenylcarbamide and nitrogen. The hydrazides in ethereal solution act in the same way as aniline under the same circumstances, azoimide and a substituted hydrazine being obtained, whilst in solution in acetone they always produce molecular change, accompanied by evolution of nitrogen,

$$Bz{\cdot}N_3 + NHBz{\cdot}NH_2 = NHPh{\cdot}CO{\cdot}NH{\cdot}NHBz + N_2.$$

Of the acid hydrazides of the bibasic acids, those of fumaric and carbonic acids behave towards nitrous acid in a similar manner to the hydrazides of the monobasic acids. Fumarhydrazide is thus converted into a frightfully explosive diazide, $C_2H_2(CO{\cdot}N_3)_2$, and carbohydrazide into carbazide, $CO(N_3)_2$, which is a crystalline, spontaneously explosive substance.

An account of the experimental researches, of the results of which the foregoing is a general statement, will be shortly published.

A. H.

Benzoylhydrazine (Benzhydrazide). By G. Struve (*J. pr. Chem.*, 1894, [2], **50**, 295—310; compare the foregoing abstract).—Benzoylhydrazine, $NHBz{\cdot}NH_2$, which was first prepared by Curtius from ethylic benzoylglycollate (Abstr., 1891, 56), may also be obtained by the action of hydrazine hydrate on ethylic benzoate, benzamide, benzoic chloride, or benzoylazoimide, BzN_3. It forms colourless plates with a silvery lustre, and melts at 112·5°. It reduces Fehling's solution, and ammoniacal silver solution in the cold, and converts platinic chloride into the platinous salt. It is very slowly attacked by dilute acids, and is still more stable towards alkalis. When rapidly heated, it boils without decomposing, but when heated for some time at 180° it decomposes with evolution of gas and formation of dibenzoylhydrazine. The *hydrochloride*, $NHBz{\cdot}NH_2,HCl$, forms small, colourless tablets, which readily dissolve in water and alcohol, and melt and decompose at about 185°. The *platinosochloride* $(NHBz{\cdot}NH_2)_2,H_2PtCl_4$, is obtained as a yellowish-white precipitate when platinous chloride is added to an alcoholic solution of benzoylhydrazine, nitrogen being evolved; it is decomposed by boiling water. *Sodium benzoylhydrazine*, prepared by the action of sodium on benzoylhydrazine suspended in xylene, or by that of sodium ethoxide on its alcoholic solution, crystallises in tablets, which are stable in the air. *Acetylbenzoylhydrazine*, N_2H_2BzAc, crystallises in colourless, lustrous plates, melting at 170°. Symmetrical dibenzoylhydrazine,

$$NHBz{\cdot}NHBz,$$

has been previously described by Curtius (Abstr., 1891, 56). It is formed when benzoylhydrazine is heated at 180°, by the action of ethylic benzoate on the hydrazide, and by the action of iodine or mercuric oxide on an alcoholic solution of the same substance. It crystallises in small, silky needles, melting at 233°. By continued boiling with dilute sulphuric acid, it is converted into benzoic acid and hydrazine sulphate.

The compounds of benzoylhydrazine with aldehydes are formed by shaking the hydrazine with the aldehyde in aqueous solution, and are scarcely soluble in water. They are insoluble in dilute acids and alkalis, but are decomposed by boiling with them. *Benzylidenebenzoylhydrazine*, $CHPh{:}N{\cdot}NHBz$, crystallises in colourless needles, melting at 202°. *Orthohydroxybenzylidenebenzoylhydrazine* forms yellowish-white needles, melting at 182°. *Metanitrobenzylidenebenzoylhydrazine* crystallises in well-developed prisms, which become red on exposure to the air, and melt at 192°. *Parahydroxybenzylidenebenzoylhydrazine* forms fascicular groups of colourless needles, melting at 233°. *Cinnamylidenebenzoylhydrazine* crystallises in small, colourless needles, and melts at 193°. *Propylidenebenzoylhydrazine* is readily soluble in hot water, and forms colourless prisms, which melt at 117°. Benzoylhydrazine does not appear to react with glucose.

The compounds of benzoylhydrazine with ketonic substances resemble the aldehydo-compounds in their general properties. The reaction with orthodiketones only proceeds when the two are heated together under pressure; and whilst the α-ketonic acids react very easily, no definite compounds have yet been obtained from the β- and γ-acids. *Acetonebenzoylhydrazone* forms colourless needles, melting at 142°. *Benzylideneacetonebenzoylhydrazone* crystallises in silky needles, and melts at 157°. *Acetophenonebenzoylhydrazone* forms colourless needles, and melts at 153°. Benzoylhydrazine reacts with isatin, forming a condensation product, $NHBz{\cdot}N{:}C\begin{<}{C_6H_4}\\{C(OH)}\end{>}N$, which crystallises in lustrous, golden-yellow plates, and melts at 279°.

With benzile, a *dihydrazone*, $NHBz{\cdot}N{:}CPh{\cdot}CPh{:}N{\cdot}NHBz$, is formed which crystallises in small, colourless needles melting at 206°. The *benzoylhydrazone of ethylic pyruvate* also crystallises in colourless needles, and melts at 155°. A. H.

Action of Nitrous Acid on Isomethyleugenol. By G. Malagnini (*Gazzetta*, 1894, **24**, ii, 1—20; compare Abstr., 1893, i, 196).—*Diisonitrosonitroisomethyleugenol peroxide*, $\begin{matrix}MeC{=}N{\cdot}O\\|\\NO_2{\cdot}C_6H_2(OMe)_2{\cdot}C{=}N{\cdot}O\end{matrix}$, is prepared by treating diisonitrosoisomethyleugenol peroxide with nitric acid; it separates on pouring the product into water, and crystallises in straw-coloured needles melting at about 189°.

The *bromo-derivative* of the peroxide, $\begin{matrix}MeC{=}N\\|\\C_6H_2Br(OMe)_2{\cdot}C{=}N\end{matrix}\!>O$, obtained by brominating the peroxide in glacial acetic acid solution, forms small, colourless crystals, melting at 133°.

Diisonitrosoisomethyleugenol peroxide, like the corresponding iso-

safrole compound, yields an *isomeride*, $C_6H_3(OMe)_2\cdot\overset{|}{C}\!=\!N\!-\!\overset{|}{O}\!-\!\overset{|}{C}(NOH)\cdot CH_2$, on warming with potash; it separates from ethylic acetate in colourless crystals, melting and decomposing at 171—172°; it is very soluble in aqueous potash, whereas the peroxide is insoluble. The *monacetyl*-derivative crystallises in white needles melting at 115°.

The peroxide is reduced by tin and hydrochloric acid, with formation of a *furazanic* compound, $C_6H_3(OMe)_2\cdot\overset{|}{C}\!=\!N\!>\!O\!<\!N\!=\!\overset{|}{C}Me$; this crystallises in stellate aggregates, melts at 75°, and is very stable. On reducing the peroxide with zinc-dust and acetic acid, the *α-dioxime*, $C_6H_3(OMe)_2\cdot C(NOH)\cdot CMe{:}NOH$, is obtained; the crystals melt at 112°, and effloresce on exposure to air. When heated for some time at a temperature a little above 112°, they are transformed into the *β*-dioxime; this melts at 196°, and resembles the *α*-compound in appearance.

The *monacetyl* derivative of the *α*-dioxime crystallises in colourless prisms melting at 98°, and yields the furazanic compound described above on heating with potash. The *acetyl* derivative of the *β*-dioxime melts at 105°, and when treated with potash is hydrolysed with regeneration of the oxime. Both the *α*- and *β*-dioximes yield diisonitrosoisomethyleugenol peroxide on oxidation with potassium ferricyanide in alkaline solution.

Isomethyleugenol nitrosite, $C_6H_3(OMe)_2\cdot\overset{|}{C}H\cdot\overset{|}{N}\!-\!\overset{|}{O}\!>\!O\!<\!\overset{|}{O}\!-\!\overset{|}{N}\cdot CHMe$, may be prepared by gradually adding dilute sulphuric acid, a few drops at a time, to a light-petroleum solution of isomethyleugenol suspended in sodium nitrite solution. It melts and decomposes at 107°, and is very unstable; on boiling with alcohol, it is converted into diisonitrosoisomethyleugenol peroxide, melting at 118°. W. J. P.

Configuration of Certain Glyoximes. By A. Angeli and G. Malagnini (*Gazzetta*, 1894, **24**, ii, 131—145).—Isosafrole-*α*-dioxime is very readily acted on by phosphorus oxychloride, yielding an *azoxime*, $\begin{matrix}CMe{:}N\\ |\\ O\!-\!N\end{matrix}\!>\!C\cdot C_6H_3{:}O_2{:}CH_2$, which forms almost colourless crystals melting at 116—117°; it is insoluble in potash, and has an odour resembling that of coumarin.

On heating piperonylonitrile in a sealed tube at 110° with hydroxylamine hydrochloride and sodium carbonate, an *amidoxime*, $NH_2\cdot C(NOH)\cdot C_6H_3{:}O_2{:}CH_2$, is obtained; it crystallises in thin, yellow needles melting at 143°. The *acetyl* derivative,

$$NH_2\cdot C(NOAc)\cdot C_6H_3{:}O_2{:}CH_2,$$

is a colourless, crystalline substance, which melts at 128°; on heating it just above its melting point, it is converted into the azoxime described above.

Isosafrole *α*-dioxime, on treatment with phosphorus pentachloride, yields the azoxime, together with *acetylpiperylcarbamide*,

$$CH_2{:}O_2{:}C_6H_3\cdot NH\cdot CO\cdot NHAc;$$

the latter crystallises in long, white needles melting at about 216°, and, on boiling with potash, yields ammonia and acetic acid.

Isosafrole-β-dioxime, when treated with phosphorus oxychloride, yields the azoxime melting at 116—117°, together with piperonylonitrile. The same products are formed on treating the β-dioxime with phosphorus pentachloride.

On warming the diacetyl-derivative of isosafrole-α-dioxime with potash, the furazanic compound obtained from isosafrole is formed; under similar conditions, the diacetyl-derivative of the β-dioxime is converted into the β-dioxime.

On heating isosafrole-α-dioxime in a closed tube with water at 160° for three hours, it is completely converted into the above-mentioned furazanic compound; the β-dioxime, when treated in like manner, yields the furazan together with the α-dioxime.

The results described above demonstrate that the α- and β-dioximes of isosafrole are compounds of the same type as the γ- and α-benzildioximes respectively. W. J. P.

Occurrence of Polymorphous Modifications of Derivatives of Hydroxylamine. By W. Lossen* (*Annalen*, 1894, **281**, 169—305; compare Abstr., 1892, 711).—*Metatoluhydroxamic acid*,

$$C_6H_4Me\cdot C(N\cdot OH)\cdot OH,$$

is obtained, together with metatoluic acid and mono- and di-hydroxamic acids, by the interaction of hydroxylamine hydrochloride, metatolnic chloride, and soda; it forms orthorhombic crystals, melting at 119—120°; $a : b : c = 0{\cdot}5381 : 1 : 0{\cdot}2908$. The *para*-isomeride is prepared in a similar manner, and crystallises in colourless, pearly, orthorhombic leaflets, melting and decomposing at 148°; $a : b = 0{\cdot}9325 : 1$.

Isophthalylhydroxamic acid, $C_6H_4[C(N\cdot OH)\cdot OH]_2$, prepared from isophthalic chloride, crystallises in spherical aggregates, melting at 192° with decomposition. The isomeric *terephthalylhydroxamic acid* crystallises in prisms melting and decomposing at 232°; its *sodium* salt, $C_8H_6N_2O_4Na_2,2H_2O$, is obtained in microscopic, flattened prisms, and explodes on heating. The *potassium hydrogen* salt, $C_8H_7N_2O_4K$, is also crystalline and explosive; the *barium* salt is insoluble in water, and, when carefully distilled to avoid explosion, yields a small proportion of paraphenylenediamine.

Alkylic salts of the mono-substituted hydroxamic acids, in which the alkyl radicle enters the oximido-group, may be prepared by three methods. By the action of an alkylic iodide on an alkali salt of the hydroxamic acid; by the action of an acid chloride on an alkylhydroxylamine; or by the hydrolysis of an alkylic alkylhydroxamate—the latter method seems to yield the best results. The *potassium* derivative, OEt·N:CPh·OK, of ethylic benzhydroxamate is described, together with the corresponding *sodium*, *barium*, *magnesium*, and *copper* compounds. Methylic benzhydroxamate is conveniently prepared by the interaction of benzhydroxamic acid and methylic

* The nomenclature of the hydroxamic acids is in a state of great confusion; the names in the abstract are those given in the original paper.—Editors.

iodide in a methylic alcohol solution of potash; it crystallises in orthorhombic plates; $a : b = 0{\cdot}924 : 1$.

Ethylic paratoluhydroxamate, $C_6H_4Me{\cdot}C(N{\cdot}OEt){\cdot}OH$, may be prepared from paratolenylethoximidoethylic ether from ethylic ethylparatoluhydroxamate; or from paratoluethylbenzhydroxylamine; it crystallises in orthorhombic prisms melting at 101°; $a : b : c = 0{\cdot}5642 : 1 : 0{\cdot}7212$.

Ethylic anishydroxamate is obtained in mono-symmetric crystals; $a : b : c = 1{\cdot}3174 : 1 : 0{\cdot}8563$. $\beta = 86° 54'$. Its *benzylic* derivative, $OMe{\cdot}C_6H_4{\cdot}C(N{\cdot}OC_7H_7){\cdot}OH$, forms monosymmetric crystals melting at 113°; $a : b : c = 0{\cdot}9314 : 1 : 0{\cdot}8231$. $\beta = 85° 10'$.

α-Ethylbenzhydroxamic acid is obtained by the action of potash on ethylic α-benzoparatoluhydroxamate, or of alcoholic ammonia on ethylic α-ethylbenzhydroxamate; the β-ethylbenzhydroxamic acid is formed from the corresponding β-isomerides of these substances. By treating α- or β-ethylbenzhydroxamic acid with paratoluic chloride, ethylic α- or β-benzparatoluhydroxamate respectively is produced. It seems not improbable that a third modification of ethylbenzhydroxamic acid can exist; an *isomeride*, melting at about 40°, is obtained in small quantities as a bye-product in several processes.

The methylbenzhydroxamic acid, which melts at 64—65°, described by Lossen and Zanni (*Annalen*, **182**, 226), is termed the α-modification; all attempts to prepare it again have failed, but it nevertheless exists, and seems to crystallise in the orthorhombic system. Its β-isomeride, which melts at 101°, may be prepared in many ways; it crystallises in large, lustrous, cubic crystals, showing pentagonal hemihedrism; its *hydrochloride* is a crystalline powder.

The α- and β-*propylbenzhydroxamic acids*, $OH{\cdot}N{:}CPh{\cdot}OC_3H_7$, are obtained at the same time when benzimidopropylic ether acts on hydroxylamine hydrochloride. The α-acid crystallises in lustrous, monosymmetric prisms, melting at 33·5°; $a : b : c = 2{\cdot}090 : 1 : 2{\cdot}133$; $\beta = 93° 3'$. The β-acid is obtained in anorthic prisms, melting at 47·5—48°; $\gamma = 76° 58'$.

An oily *ethylmetatoluhydroxamic acid* is obtained by treating ethylic dimetatoluhydroxamate with potash.

The α- and β-*ethylparatoluhydroxamic acids*, $C_6H_4Me{\cdot}C(N{\cdot}OH){\cdot}OEt$, may be prepared by several methods. The α-acid is obtained crystalline with difficulty, and melts at 34°; its *hydrochloride* was prepared. The β-acid crystallises in large, anorthic tablets or prisms, melting at 103°; $a : b : c = 0{\cdot}797 : 1 : 0{\cdot}459$. $\alpha = 93° 1'$; $\beta = 101° 53'$; $\gamma = 88° 56'$.

The α- and β-*ethylanishydroxamic acids*, $OMe{\cdot}C_6H_4{\cdot}C(N{\cdot}OH){\cdot}OEt$, may be prepared in several ways; the α-acid crystallises in thin, monosymmetric plates melting at 49°. The β-isomeride crystallises in monosymmetric needles; $a : b : c = 1{\cdot}4693 : 1 : 1{\cdot}4043$. $\beta = 72° 27{\cdot}5'$. It melts at 97°.

Methylanishydroxamic acid, $OMe{\cdot}C_6H_4{\cdot}C(N{\cdot}OH){\cdot}OMe$, crystallises well, and melts at 113·5°.

The same methylic salt is obtained from both α- and β-ethylbenzhydroxamate; it melts at 151°. *Methylic methylbenzhydroxamate* is a highly refractive liquid boiling at 216—217°.

Ethylic ethylparatoluhydroxamate is obtained as a mobile oil, boiling at 150—155° under a low pressure; the *methylic* salt and *ethylic methylanishydroxamate* were also prepared.

Dimetatoluhydroxamic acid, $C_7H_7{\cdot}C(NO{\cdot}CO{\cdot}C_7H_7){\cdot}OH$, is obtained during the preparation of metatoluhydroxamic acid; it crystallises in monosymmetric tablets; $a : b : c = 0{\cdot}8201 : 1 : 1{\cdot}3871$. $\beta = 108°\ 45'$. It melts at 95·5°. The *ethylic* salt is an oily liquid, having a sp. gr. of 1·1160 at 15°. The isomeric *dipara*-acid crystallises in monosymmetric pyramids melting at 167°; $a : b : c = 1{\cdot}3554 : 1 : 3{\cdot}1580$. $\beta = 87°\ 53{\cdot}5'$. The *α-ethylic* salt is prepared from the silver salt, and crystallises in anorthic plates or prisms melting at 78°; $a : b : c = 0{\cdot}9059 : 1 : 1{\cdot}2160$. $\alpha = 80°\ 52'$; $\beta = 101°\ 1'$; $\gamma = 110°\ 10'$. An isomeric *β-ethylic* salt is obtained by the action of paratoluic chloride on *α-* or *β*-ethylparatoluhydroxamic acid; it crystallises in monosymmetric plates melting at 54°. Both salts yield the acid on hydrolysis with hydrochloric acid.

Benzparatoluhydroxamic acid, $OH{\cdot}CPh{:}NO{\cdot}CO{\cdot}C_7H_7$ is prepared by hydrolysis of its *α-* or *β*-ethylic salt or by the action of paratoluic chloride on benzhydroxamic acid; it forms monosymmetric tablets melting at 155°. $a : b : c = 1{\cdot}4312 : 1 : 2{\cdot}2083$. $\beta = 65°\ 25'$. The *α-ethylic* salt is obtained from the silver salt or by the action of paratoluic chloride on *α*-ethylbenzhydroxamic acid; it forms anorthic crystals melting at 114·5°; $a : b : c = 0{\cdot}8494 : 1 : 1{\cdot}0058$. $\alpha = 88°\ 23{\cdot}5'$; $\beta = 101°\ 35'$; $\gamma = 119°\ 3'$. The *β-ethylic* salt, prepared from *β*-ethylbenzhydroxamic acid, crystallises in monosymmetric tablets melting at 70°; $a : b : c = 1{\cdot}0882 : 1 : 0{\cdot}6851$. $\beta = 84°\ 35'$.

Paratolubenzhydroxamic acid, $C_7H_7{\cdot}C(NO{\cdot}COPh){\cdot}OH$, melts at 156°. The *α-ethylic* salt, prepared from the silver salt or from *α*-ethylparatoluhydroxamic acid, forms monosymmetric crystals melting at 62°; $a : b = 1{\cdot}3040 : 1$. $\beta = 68°\ 23'$. The *β-isomeride*, prepared from *β*-ethylparatoluhydroxamic acid, is also monosymmetric, and melts at 51·5—52°; $a : b : c = 1{\cdot}0766 : 1 : 1{\cdot}8364$. $\beta = 83°\ 50'$. A third *γ-isomeride*, melting at 56°, accompanies the *α*-salt; the oily residue obtained after separation of this, together with the solid salts, yields *β*-ethylparatoluhydroxamic acid on treatment with potash.

Isophthalylbenzhydroxamic acid, $C_6H_4[C(NO{\cdot}COPh){\cdot}OH]_2$, prepared from benzoic chloride and isophthalylhydroxamic acid, crystallises in white needles melting at 162°; the *potassium* salt, $C_{22}H_{14}N_2O_6K_2$, is readily converted into metaphenylenecarbamide in aqueous solution. The isomeric *terephthalylbenzhydroxamic acid* crystallises in leaflets melting at 198°; its *potassium* salt is readily hydrolysed with formation of paraphenylenecarbamide.

Dibenzhydroxamic acid is formed by the action of dry hydrogen chloride on benzhydroxamic acid; the fact explains the formation of the former acid during the decomposition of the hydrochlorides of alkylhydroxamic acids. Both *α-* and *β*-ethylic dibenzhydroxamate have the normal molecular weight in freezing phenol. The oily product of the action of methylic iodide on silver dibenzhydroxamate, which has previously been considered as the methylic salt, yields a crystalline *α-methylic dibenzhydroxamate* by suitable treatment; the salt crystallises in orthorhombic prisms melting at 53—54°; $a : b =$

0·9713 : 1. The *β-methylic* salt is obtained by the action of benzoic chloride on β-methylbenzhydroxamic acid; it forms anorthic crystals melting at 55·3°; $a : b : c = 1·6108 : 1 : 0·7226$. $\alpha = 115° 24'$; $\beta = 112° 41'$; $\gamma = 76° 10'$. The two salts yield β-methylbenzhydroxamic acid on hydrolysis. The *α-propylic* salt, prepared by the action of propylic iodide on silver dibenzhydroxamate, crystallises in orthorhombic prisms melting at 32°. It is accompanied by the *γ-propylic* salt (?) which melts at 20·5—24°. *β-Propylic dibenzhydroxamate* is prepared from propylbenzhydroxamic acid; it crystallises in the anorthic system, and melts at 50·3°; $a : b : c = 1·9767 : 1 : 0·7758$. $\alpha = 90° 52'$; $\beta = 98° 8'$; $\gamma = 84° 33'$. All three isomerides yield β-propylbenzhydroxamic acid on hydrolysis.

α-Ethylic benzparatoluhydroxamate, $CPh·C(NO·CO·C_7H_7)·OEt$, prepared by methods similar to those employed for the preceding α-salt, crystallises in the anorthic system, and melts at 114·5°; $a : b : c = 0·8494 : 1 : 1·0058$. $\alpha = 88° 23·5'$; $\beta = 101° 35'$; $\gamma = 119° 3'$.

The *β-isomeride* crystallises in monosymmetric tablets melting at 70°; $a : b : c = 1·0882 : 1 : 0·6851$. $\beta = 84° 35'$. The salts yield benzparatoluhydroxamic acid on acid hydrolysis, and α- and β-ethylbenzhydroxamic acid respectively on hydrolysis with potash. The *α-methylic* salt crystallises in the anorthic system, and is crystallographically similar to the α-ethylic salt; it melts at 108·5°; $a : b : c = 0·8006 : 1 : 1·0756$. $\alpha = 86° 8·5'$; $\beta = 99° 10'$; $\gamma = 120° 19·5'$. The *β-methylic* salt is also anorthic, and melts at 65°; $a : b = 1·4907 : 1$. $\alpha = 104° 25'$; $\beta = 113° 50'$; $\gamma = 96° 23'$.

α-Ethylic paratolubenzhydroxamate, $C_7H_7·C(NO·COPh)OEt$, crystallises in monosymmetric prisms melting at 62°; $a : b = 1·3040 : 1$. $\beta = 68° 22'$. The β-salt forms monoclinic crystals, $a : b : c = 1·0766 : 1 : 1·8364$. $\beta = 83° 50'$. It melts at 51·5—52°. The *γ-salt* melts at 56°, and is separated from an oily residue which has the same composition.

α-Ethylic dianishydroxamate, $C_7H_7O·C(NO·CO·C_7H_7O)OEt$, crystallises in orthorhombic prisms melting at 94°;

$$a : b : c = 0·8820 : 1 : 0·3970.$$

The *β-salt* is obtained in anorthic crystals melting at 77°; $a : b : c = 0·5971 : 1 : 1·2595$. $\alpha = 89° 4'$; $\beta = 100° 43'$; $\gamma = 128° 45'$. The *α-methylic* salt forms orthorhombic leaflets melting at 50—51°, whilst the *β-isomeride* crystallises in needles melting at 91°.

α-Ethylic anisbenzhydroxamate, $C_7H_7O·C(NO·COPh)·OEt$, forms anorthic crystals melting at 79° (*Annalen*, **217**, 7); $a : c = 1 : 0·7234$. $\alpha = 109° 29·5'$; $\beta = 124° 14'$; $\gamma = 62° 23·5'$. The *β-isomeride* crystallises in monosymmetric tablets melting at 51°; $a : b : c = 0·6009 : 1 : 0·3302$. $\beta = 89° 7·5'$. The *α-methylic* salt, prepared from the silver salt, crystallises in monosymmetric tablets melting at 96°; $a : b : c = 1·0304 : 1 : 0·8644$. $\beta = 85° 54·5'$. It is accompanied by the *β-isomeride*, which crystallises in needles melting at 89°.

The following seven derivatives are obtained by the action of acid chlorides on the metallic derivatives of the alkylic salts of substituted hydroxamic acids.

Benzethylacethydroxylamine, $CPh(NOEt)·OAc$, prepared from acetic chloride and ethylic argentobenzhydroxamate, crystallises

in prisms melting at 55°; it yields ethylic benzhydroxamate on hydrolysis with baryta.

Benzethylcarbethoxyhydroxylamine, $CPh(N{\cdot}OEt)O{\cdot}COOEt$, prepared by the action of ethylic chlorocarbonate on ethylic potassiobenzhydroxamate, crystallises in plates melting at 40°.

Benzethylsuccinylhydroxylamine, $C_2H_4(COO{\cdot}CPh{:}NOEt)_2$, crystallises in plates melting at 60°; it yields succinic acid on hydrolysis, and on heating above its melting point yields phenylic cyanate and ethylic succinate.

Benzethylphthalhydroxylamine, $C_6H_4(COO{\cdot}CPh{:}NOEt)_2$, crystallises in prisms melting at 54°.

Benzethylparatoluhydroxylamine, $CPh(NOEt)O{\cdot}CO{\cdot}C_7H_7$, and *paratoluethylbenzhydroxylamine* are obtained as viscid liquids. *Paratoluethyltoluhydroxylamine* crystallises in the orthorhombic system, and melts at 70·5°; $a : b : c = 0{\cdot}6805 : 1 : 0{\cdot}7604$.

The following triacidylhydroxylamines have the normal molecular weight in freezing phenol solution.

γ-Tribenzhydroxylamine (compare *Annalen*, **186**, 35) crystallises in the monosymmetric system; $a : b : c = 0{\cdot}9366 : 1 : 1{\cdot}4855$. $\beta = 65° 33'$. The α-, β-, and γ-isomerides all give the same benzhydroxamic acid with alcoholic ammonia and the same dibenzhydroxamic acid on hydrolysis with hydrochloric acid; they also all three yield benzoic anhydride and phenylic cyanate on heating. If the heating is too prolonged, benzanilide is formed by the action of the phenylic cyanate on the benzoic anhydride. The α- and γ-modifications are converted into the β-isomeride on warming with hydrochloric acid. The three isomerides yield *ammonium hydrogen benzhydroxamate*, $C_7H_6NO_2{\cdot}NH_4, C_7H_7NO_2$, on treatment with alcoholic ammonia; this crystallises well, melts at 146°, is very characteristic, and loses ammonia over sulphuric acid or at 100°.

α-Dibenzparatoluhydroxylamine, $C_7H_7{\cdot}COO{\cdot}CPh{:}NO{\cdot}COPh$, is prepared by the action of paratoluic chloride on silver dibenzhydroxamate; it crystallises in monosymmetric needles melting at 131·5°, and is crystallographically similar to α-tribenzhydroxylamine; $a : b : c = 1{\cdot}4127 : 1 : 1{\cdot}1326$. $\beta = 81° 36{\cdot}5'$. It is accompanied by a *β-isomeride* (?), which melts at 104°.

Isomerides of the following amidoximes could not be prepared.

Benzenylamidoxime methylic ether (compare Abstr., 1889, 1064) crystallises in the monosymmetric system; $a : b : c = 2{\cdot}717 : 1 : 2{\cdot}116$. $\beta = 121° 52'$. The corresponding *propylic ether*, $CPh(NO{\cdot}C_3H_7)NH_2$, prepared by the action of sodium propoxide and propylic iodide on benzenylamidoxime, is crystallographically similar to the preceding, and melts at 27°.

Paratolenylamidoxime ethylic ether (compare Schubart, Abstr., 1890, 47) is monosymmetric; $a : b : c = 0{\cdot}539 : 1 : 0{\cdot}272$. $\beta = 69°$. The corresponding methylic ether is also monosymmetric.

Anisenylamidoxime ethylic ether (compare Miller, Abstr., 1890, 144) is obtained in monosymmetric crystals;

$$a : b : c = 0{\cdot}8080 : 1 : 0{\cdot}9357. \quad \beta = 86° 9'.$$

The above results show that the only classes of hydroxylamine

derivatives readily obtained in polymorphous modifications, are the alkylhydroxamic acids, the alkylic dihydroxamates, and the triacidylhydroxylamines; polymorphism may be regarded as a general property of these substances. Polymorphism is never observed amongst the hydroxamic acids, the alkylic hydroxamates or the dihydroxamic acids. These substances may be prepared by a number of different methods—thus, the same benzhydroxamic acid is obtained from α- and β-ethylbenzhydroxamic acid, and from the α-, β-, and γ-tribenzhydroxylamines—the probability of the occurrence of polymorphism amongst these substances is therefore very small. It would also seem that alkylic acidylhydroxamates only occur in one modification, although here the experimental evidence is not so extensive as in the preceding cases. In certain classes three modifications of some of the substances may be obtained; it may consequently be supposed that each of these substances is trimorphous, although whether this also holds for those groups in which not more than two modifications have been observed is of course still uncertain. The crystallographic examination of compounds of the same type shows that there is in many cases a great similarity between them; no conclusions of importance, however, can be drawn from this fact.

After referring to Hantzsch and Werner's stereochemical hypothesis (Abstr., 1892, 461), the author points out that in those substances which exhibit polymorphism there is always one carbon atom, which is attached to four different radicles; by the change of orientation of this carbon atom, three different configurations of the same structural formula can be devised. It is, however, not improbable that the differences between the various modifications of the above substances are structural differences. Much may be said in favour of assigning the structurally different constitutions, $CPh{\cdot}C(OEt){:}N{\cdot}OH$ and $CPh{\cdot}C(OEt)<\overset{NH}{\underset{O}{|}}$, to the two ethylbenzhydroxamic acids, and the properties of the three ethylic paratolubenzhydroxamates seem to be satisfactorily explained by the following three formulæ,

$$C_7H_7{\cdot}C(OEt){:}N{\cdot}O{\cdot}COPh,\ C_7H_7{\cdot}C(OEt)<\overset{N{\cdot}COPh}{\underset{O}{|}},\ \text{and}$$

$$C_7H_7{\cdot}C(OEt)<\overset{-N-}{\underset{O{\cdot}CPh}{|}}>O.$$

W. J. P.

Space Isomerism of Carbodiphenylimides and Carboditolylimides. By C. Schall (*Ber.*, 1894, **27**, 2696—2700).—The author gives reasons for regarding the three modifications of each of these diimides as really isomeric, and not polymeric (compare Abstr., 1892, 1452; 1893, i, 701). The fourth (δ) modification of carbodiphenylimide, previously described, has been found to be a mixture of the β-diimide with triphenylguanidine. C. F. B.

Synthesis of Piperic acid and Piperine. By A. Ladenburg and M. Scholtz (*Ber.*, 1894, **27**, 2958—2960).—Piperonal does not condense with crotonaldehyde, but with acetaldehyde in presence of

alkali it yields *piperonalacraldehyde*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CHO$, which crystallises in yellow plates, melts at 70°, boils at 180—190° (20 mm.), and has a slight aromatic odour. The *phenylhydrazone* forms yellow crystals, melts at 160°, and turns brown on exposure to light. The *anilide* crystallises in pale yellow needles melting at 118°. Piperic acid is formed by fusing piperonalacraldehyde with anhydrous sodium acetate and acetic anhydride; it is identical with the natural acid. The following salts were prepared from both acids, and were found to agree in properties:—The *potassium salt* crystallises in lustrous needles; the *sodium salt* is crystalline; the *calcium*, *barium*, and *magnesium salts* appear as if they were amorphous, but in reality consist of slender, microscopic needles; the *manganous salt* crystallises in lustrous, yellow plates, the *copper salt* in slender, blue, stellate needles. The *lead salt* is amorphous. J. B. T.

Action of Methylic Iodide on Potassium Resacetophenone. By G. Gregor (*Monatsh.*, 1894, **15**, 437—445).—It has recently been shown by Wechsler (Abstr., 1894, i, 521) that potassium resacetophenone is converted by the action of ethylic iodide into diethoxyacetophenone, both ethyl groups being present as ethoxy-groups. The author has continued the investigation, with the view of discovering whether any other compounds are formed in the action, and also to ascertain if analogous products could be obtained by the action of methylic iodide.

By the action of ethylic iodide on potassium resacetophenone, the author has obtained, in addition to the diethyl derivative, a *monethyl*-derivative, $C_8H_7O_2{\cdot}OEt$, which can be separated from the crude product by shaking the ethereal solution with potash. It crystallises in long, colourless needles, melts at 48°, and, with ferric chloride, gives a reddish-brown coloration with a tinge of violet.

The methylic derivatives are prepared by boiling a solution of resacetophenone and potash in methylic alcohol with methylic iodide, distilling off the alcohol, mixing with water, and extracting with ether. The ethereal solution is shaken with potash to remove phenolic compounds, and the oil which remains on evaporating the ethereal solution is dissolved in alcohol and precipitated with water. Two products are thus obtained, one separating in crystals and the other as an oil. The former is a mixture of a methyl- and dimethyl-resacetophenone, which may be separated by crystallisation from light petroleum, the monomethyl-derivative being present in small quantity only. The *dimethyl*-derivative is thus obtained in colourless plates; it melts at 80—81°, and only contains one methoxyl group; hence the compound has the constitution $C_6H_6O_2Me{\cdot}OMe$. The substance which separates as an oil on adding water to the alcoholic solution has the composition of a dimethylresacetophenone, but the determination of the number of methoxyl groups shows that it is not homogeneous, but consists probably of a mixture of dimethoxyacetophenone with another dimethyl derivative.

The portion of the product which was soluble in alkali consists chiefly of the *monomethyl*-derivative, which, after crystallisation from alcohol, melts at 49°, and is coloured dark reddish-brown by ferric

chloride. It has the composition $C_9H_{10}O_3$, and contains one methoxyl group, and is therefore methoxy acetophenone, $C_6H_7O_2{\cdot}OMe$.

H. G. C.

Gallacetophenone. By M. Nencki (*Ber.*, 1894, **27**, 2737—2738).—The acetyl-group in gallacetophenone, chlorogallacetophenone, and gallobenzophenone has probably the same position as the carboxyl group in pyrogallolcarboxylic acid, namely is adjacent to an hydroxyl group. The three ketones named above all behave towards sulphuric acid in a similar manner to pyrogallolcarboxylic acid, a violet coloration being produced when sulphuric acid containing a trace of nitric acid is added to a dilute solution of the compound in sulphuric acid.

Chlorogalloacetophenone, moreover, is converted, by treatment with calcium carbonate, into the anhydroglycogallol, $C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2Cl = C_6H_2(OH)_2{<}\overset{O}{\underset{CO}{>}}CH_2 + HCl$. This behaviour is not shown by such compounds as chloracetocatechone, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2Cl$ [OH : OH : $COCH_2Cl$ = 1 : 2 : 4], in which the chloracetyl group is not in the ortho-position to any of the hydroxyl-groups.

A. H.

Interaction of the Sodium Derivatives of Phenol with Ethylic Monochloracetate and Dichloracetate. By K. Auwers and K. Haymann (*Ber.*, 1894, **27**, 2795—2806; compare Bischoff and Walden, Abstr., 1894, i, 403).—*Ethylic diphenoxyacetate*, $CH(OPh)_2{\cdot}COOEt$, prepared by heating phenol, ethylic dichloracetate, and sodium in alcoholic solution, is a pale yellow oil, which is readily hydrolysed by soda, and boils at 208° (28 mm.), 229° (41 mm.), or at 240° (53 mm.); the yield is 60 per cent. of the theoretical. The *acid* crystallises from glacial acetic acid in silky, lustrous needles, melts at 91°, and is less soluble in water than phenoxyacetic acid. The *silver*, *lead*, *zinc*, and *copper salts* are sparingly soluble; the *sodium salt* is crystalline. The *amide* crystallises in lustrous plates, melts at 108°, and in benzene solution gives abnormal cyroscopic results. The yield is almost quantitative. *Dibromodiphenoxyacetic acid*, $CH(O{\cdot}C_6H_4Br)_2{\cdot}COOH$, formed by the action of aqueous bromine on the acid in glacial acetic acid solution, crystallises in slender needles melting at 151°. The *silver* and *sodium salts* are sparingly soluble; the former darkens on exposure to light. Diphenoxyacetic acid resembles phenoxyacetic acid in its behaviour towards nitric acid; it is scarcely attacked by dilute acid (sp. gr. 1·3), but with the concentrated acid yields nitrophenols.

Ethylic di-α-naphthoxyacetate, $CH(O{\cdot}C_{10}H_7)_2CO{\cdot}OEt$, prepared in a similar manner to the phenoxy-derivative, is a viscid oil, and decomposes when distilled. The *acid* crystallises in lustrous prisms, and melts at 174°. The *sodium salt* crystallises in lustrous, concentric needles. *Ethylic di-β-naphthoxyacetate* resembles the α-derivative in properties and mode of preparation. The *acid* crystallises in prisms, and melts at 134°. The *sodium salt* is crystalline.

Ethylic orthobromophenoxyacetate, $C_6H_4Br{\cdot}O{\cdot}CH_2{\cdot}COOEt$, prepared from orthobromophenol, ethylic chloracetate, and sodium ethoxide, boils at 160—170° (16 mm.). The *acid* crystallises in pearly, lustrous plates, melts at 142·5—143°, and decomposes when distilled.

Attempts to eliminate hydrogen bromide by the action of alkalis, under varied conditions, were unsuccessful. The *amide* crystallises in colourless plates, melts at 151°, and boils at 250—300° under the ordinary pressure.

Methylic salicylate and ethylic chloracetate combine, forming an oily, ethereal salt, which, on hydrolysis, yields salicyloacetic acid, $COOH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}COOH$; this crystallises from benzene in needles, from water in pearly, lustrous plates, and melts at 191·5—192°, not at 186—187° as stated by Rössing, who prepared it by the oxidation of orthaldehydophenoxyacetic acid.

Guaiacol readily combines with ethylic chloracetate and ethylic dichloracetate; *ethylic guaiacolglycollate*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}COOEt$, formed in the latter case, is a colourless, oily liquid boiling at 175—179° (27 mm.). The acid has recently been described by Cutolo (Abstr., 1894, i, 289); the *amide* is deposited from benzene in colourless, lustrous, concentric crystals melting at 138°.

Dibromonitrophenol [OH : Br : NO_2 : Br = 1 : 2 : 4 : 6], ortho- and para-nitrophenols, and ortho- and para-hydroxybenzoic acids, do not react with ethylic chloracetate; resorcinol has little action on ethylic dichloracetate, and ortho- and para-nitrophenol none; thiophenol and ethylic dichloracetate yield phenylic bisulphide.

The authors have postponed the full investigation of their subject until the completion of Bischoff and Walden's work (*loc. cit.*). The above results show the great influence exerted by a second negative group in the benzene nucleus; its position and nature, whether nitro-, carboxyl-, or hydroxyl-, are of little importance, and the presence of a halogen atom in the benzene ring does not appear to affect the reaction. J. B. T.

Constitution of Phloretin. By Mrs. H. A. Michael (*Ber.*, 1894, **27**, 2686—2689).—When phloretin is treated with acetic anhydride in the presence of a little zinc chloride, anhydrous sodium acetate, or stannic chloride, it yields a *triacetyl*-derivative melting at 93·5—94·5°, not a diacetyl derivative as Schiff (*Annalen*, 156, 1) thought. If the mixture is heated for 2—3 hours, a substance melting at 166—167° is formed, probably a condensation product of phloretin. Phloretin itself is probably the phloroglucinol salt of phloretic acid, with the formula $OH{\cdot}C_6H_4{\cdot}C_2H_4{\cdot}COO{\cdot}C_6H_3(OH)_2$. C. F. B.

Ethylic Isophthalodicyanacetate. By J. Locher (*Compt. rend.*, 1894, **119**, 274—276).—*Ethylic isophthalodicyanacetate* is obtained in the same way as the terephthalic derivative (Abstr., 1894, i, 593) by the action of isophthalic chloride on ethylic sodiocyanacetate in presence of ether. It forms white microscopic needles which melt at 191—192°; it is insoluble in water, but very soluble in chloroform, and also dissolves in other organic solvents. Boiling water, alkalis, and strong acids decompose it with formation of isophthalic acid and ethylic cyanacetate.

Ethylic isophthalodicyanacetate acts as a bibasic acid, and can be titrated in dilute alcoholic solution with phenolphthaleïn as indicator. The disilver derivative is a white amorphous powder which is insoluble in water and becomes black when exposed to light; the cupric deriva-

tive forms green crystals containing $2H_2O$, which is given off in a vacuum; the ferric derivative is a brownish red crystalline powder insoluble in water and organic solvents; the ammonium salt is a white crystalline powder which dissolves in water, and melts and decomposes at 130—133°.

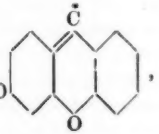
The dimethyl-derivative, $C_6H_4[CO\cdot CMe(CN)\cdot COOEt]_2$, is easily obtained by the action of methylic iodide on the silver derivative in presence of methylic alcohol. It crystallises from methylic alcohol in brilliant white microscopic needles which melt at 188°, and are insoluble in water and solutions of alkalis, but dissolve in organic solvents.

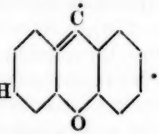
The dihydrazone is readily obtained in the same way as the para-derivative, and crystallises from alcohol in white microscopic needles which melt at 260—261°, and become red on exposure to air. It is very slightly soluble in all organic solvents, and is insoluble in water, but is decomposed by hot water, alkalis, and acids.

The author has been unable to obtain the meta- and para-derivatives corresponding to the orthophthalomonocyanacetate described by Muller. C. H. B.

Action of Aniline Bases on Benzoïn. By B. Lachowicz (*Monatsh.*, 1894, **15**, 402—403).—A recent publication by Japp and Murray (Abstr., 1894, i, 90) has led the author to revise his previous work (*ibid.*, 39). He now finds that $\alpha\beta$-diphenylanilindole, which melts at 125°, results from the interaction of aniline hydrocloride and benzoïnanilide, whilst paratoluidine hydrochloride and benzoïnanilide give rise to the same product, and, in addition to $\alpha\beta$-diphenylparatoluindole, which melts at 155°. The last-named product also results from the interaction of paratoluidine hydrochloride and benzoïnparatoluidide, whilst aniline hydrochloride and benzoïnparatoluindole yield both the indoles, and these can be separated by repeated recrystallisation. G. T. M.

Fluoresceïn Colouring Matters. By R. Möhlau and P. Koch (*Ber.*, 1894, **27**, 2887—2897).—The author applies the name of *fluorone* to substances containing the group I, and of *fluorime* to the corresponding imides, II; the name of the acid or aldehyde from which the central CR group in each compound is supposed to be derived being prefixed.

I. 

II. 

Formaldehydehydroxyfluorone, $C_6H_3O\langle\begin{matrix}CH\\O\end{matrix}\rangle C_6H_3\cdot OH$, is formed when diresorcinylmethane (Abstr., 1892, 856) is warmed with concentrated sulphuric acid, or zinc chloride and a little aluminium chloride, but has not been obtained quite pure. It is readily soluble in alkalis, the dilute solutions having an intense green fluorescence. The *diorcinylmethane* ("methylenediorcinol"), $CH_2[C_6H_2Me(OH)_2]_2$,

was obtained by the action of formaldehyde on orcinol in the presence of sulphuric acid. It forms small white crystals, is insoluble in water, and, when heated, decomposes without melting. *Formaldehydehydroxytolufluorone*, $C_6H_2MeO\lessdot^{CH}_{O_}\!>C_6H_2Me{\cdot}OH$, prepared from diorcinylmethane, separates from methylic alcohol in dark-brown, crystalline granules. Its solutions in alkalis have a yellowish-green fluorescence.

The product of the condensation of acetaldehyde with resorcinol appears to be a mixture of two different substances, formed by the interaction of the two in different proportions, but may be used for the preparation of *acetaldehydehydroxyfluorone*,

$$C_6H_3O\lessdot^{CMe}_{O_}\!>C_6H_3{\cdot}OH,$$

which is a yellowish-brown substance resembling the formaldehyde-compound in properties.

Acetaldehyde also reacts with orcinol, but it has not been found possible to obtain the condensation product or the corresponding fluorone in the pure state.

Dimethylmetamidophenol reacts with acetaldehyde in the presence of hydrochloric acid to form *ethylidenetetramethyldimetamidophenol* $CMe[C_6H_3(OH){\cdot}NMe_2]_2$, which is a light-violet coloured crystalline substance, melts at 140°, and is soluble in acids and alkalis. When this substance is heated with sulphuric acid, *tetramethyldiamidodiphenylethylidene oxide* is formed and may be precipitated by caustic soda as a violet coloured mass. On oxidation with ferric chloride or sodium nitrite in presence of hydrochloric acid, a salt of *acetaldehydetetramethylamidofluorimium hydrochloride* is formed and may be salted out in the usual way; zinc chloride precipitates the zinc double salt. Alkalis added to the solution of the colouring matter precipitate the *colour base*, which is a dark violet, crystalline mass, melting at 152°. Its solutions in dilute acids are red, and show a strong yellow fluorescence. When dried over sulphuric acid, the base has the composition required by the formula

$OH{\cdot}NMe_2{:}C_6H_3\lessdot^{CMe}_{O_}\!>C_6H_3{\cdot}NMe_2$. The *chloride* and *sulphate* are very soluble, the *picrate* and *iodide* sparingly soluble. The *platinochloride* forms dark plates with green metallic lustre. Formaldehyde condenses with dimethylamidophenol in a similar manner, producing *tetramethyldiamidodihydroxydiphenylmethane*, which crystallises in small violet plates melting at 175°. When treated with dehydrating and oxidising agents it yields *formaldehydetetramethylamidofluorimum chloride*, the zinc double salt of which is known commercially as pyronine (German patent, No. 59003). A. H.

Compounds containing the Group $C_nH_2O_2$. By A. Angeli (*Gazzetta*, 1894, **24**, ii, 59—67; compare Abstr., 1893, i, 355).—The author discusses the constitutions of compounds containing the group $C_nH_2O_2$ and their derivatives, which he has investigated.

W. J. P.

1 : 5-Diketones. By E. KNOEVENAGEL (*Annalen*, 1894, **281**, 25—126; compare Abstr., 1893, i, 419 and 697).—Symmetrical derivatives of this type are obtained by the condensation of aldehydes with ethylic acetoacetate and analogous compounds under the influence of primary and secondary amines (Hantzsch), whilst unsymmetrical 1 : 5-diketones are prepared by the addition of substances containing salt-forming methylenic hydrogen to unsaturated compounds, in the presence of sodium ethoxide or primary and secondary amines. The formation of pyridine derivatives by the action of hydroxylamine on 1 : 5-diketones is limited to those which do not undergo the intramolecular condensation already described (*loc. cit.*).

Ketophenylparacophenone, $O<\begin{matrix}CO\cdot CO\\CHPh\end{matrix}>CH\cdot COPh$ (compare W. Wislicenus, Abstr., 1893, i, 714), is obtained by saturating a well-cooled mixture of ethylic benzoylpyruvate and benzaldehyde with hydrogen chloride. When warmed with strong potash, a solution exhibiting yellow fluorescence is produced, and benzaldehyde is eliminated. It melts at 212°, and prolonged exposure to the temperature 220—230° causes it to become deep red, equal volumes of carbonic oxide and anhydride being evolved; the residual oil yields benzylideneacetophenone when distilled in a vacuum. Brought in contact with deoxybenzoïn in presence of sodium ethoxide, ketophenylparacophenone gives rise to *deoxybenzoïnbenzylideneacetophenone*, $COPh\cdot CH_2\cdot CHPh\cdot CHPh\cdot COPh$, which melts at 189°; it is also formed by mixing together the alcoholic solutions of benzylideneacetophenone and deoxybenzoïn with sodium ethoxide. On heating it with hydroxylamine hydrochloride (2—3 mols.) in dilute alcoholic solution for four hours at 140—150°, 2 : 4 : 5 : 6-*tetraphenylpyridine* is formed, which crystallises in colourless needles melting at 179°, whilst the *oxime* of deoxybenzoïnbenzylideneacetophenone is produced when the constituents are heated together for two hours on the water bath; this melts at 212°, and yields 2 : 4 : 5 : 6-tetraphenylpyridine under the influence of hydrogen chloride.

Ethylic benzylidenedibenzoylpyruvate, $CHPh(CHBz\cdot CO\cdot COOEt)_2$, is prepared by adding a few drops of diethylamine or piperidine to a mixture of benzaldehyde and ethylic benzoylpyruvate (2 mols.); it melts at 162°. When boiled with water, one molecular proportion of ethylic benzoylpyruvate is eliminated, with formation of ketophenylparacophenone.

Ethylic benzylidenedibenzoylacetate (Buchner and Curtius, Abstr., 1885, 1238) is produced by the condensation of ethylic benzoylacetate with benzaldehyde under the influence of diethylamine; it melts at 95°. *Ethylic* 2 : 4 : 6-*triphenylpyridine*-3 : 5-*dicarboxylate*, which melts at 146°, is obtained from it by heating with hydroxylamine for four hours at 120—130°.

Ethylic methylenedibenzoylacetate, $CH_2(CHBz\cdot COOEt)_2$, melting at 86°, is prepared by adding a few drops of diethylamine to a mixture of ethylic benzoylacetate and formaldehyde solution.

Ethylic 3 : 5-*diphenyl*-Δ_2-*ketotetrahydrobenzene*-6-*carboxylate*,

$$CPh<\begin{matrix}CH_2\cdot CHPh\\CH\text{——}CO\end{matrix}>CH\cdot COOEt,$$

is obtained by the interaction of ethylic acetoacetate and benzylideneacetophenone in presence of sodium ethoxide; it melts at 109°. When heated with dilute hydrochloric acid for four hours at 160°, it yields 3 : 5-*diphenyl*-Δ_2-*ketotetrahydrobenzene*, which melts at 70—72.°

Deoxybenzoïnparacinnamylanisoïl (*deoxybenzoïnbenzylideneparamethoxyacetophenone*), $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}COPh$, is obtained by adding alcoholic potash to a mixture of cinnamylanisoïl and deoxybenzoïn in molecular proportion; it melts at 206°. Substituting ethylic malonate for deoxybenzoïn, the *compound* $C_{19}H_{18}O_6$ is formed, melting at 166°, whilst benzylic cyanide gives rise to the *compound* $C_{24}H_{22}O_4$ when heated with cinnamylanisoïl and hydrochloric acid for two hours at 120°; this melts at 201°.

Ethylic deoxybenzoïnbenzylideneacetoacetate,

$$COOEt{\cdot}CHAc{\cdot}CHPh{\cdot}CHPh{\cdot}COPh$$

is obtained by adding sodium ethoxide to a mixture of ethylic benzylideneacetoacetate and deoxybenzoïn in molecular proportion dissolved in alcohol; it melts at 123°. The action of hydroxylamine on this substance gives rise to an *oxime* of the constitution

$$CHPh\begin{matrix}<\\>\end{matrix}\begin{matrix}CH(COOEt){\cdot}C(:NOH)\\CHPh\text{———}CPh\end{matrix}\begin{matrix}>\\<\end{matrix}CH,$$

in place of a pyridine derivative, two molecules of water having been eliminated instead of three. This oxime melts and decomposes at 150—155°.

Ethylic 3 : 4 : 5-*triphenyl*-Δ_2-*ketotetrahydrobenzene*-6-*carboxylate*,

$$CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CPh\text{——}CHPh\\CO{\cdot}CH(COOEt)\end{matrix}\begin{matrix}>\\<\end{matrix}CHPh,$$

is prepared by passing hydrogen chloride through alcohol in which ethylic deoxybenzoïnbenzylideneacetoacetate is suspended; it melts at 184°. When boiled for several hours with alcoholic potash (rather more than 2 mols.), it is converted into iso-3 : 4 : 5-triphenyl-Δ_2-ketotetrahydrobenzene, which melts at 138°; this is also formed on boiling a mixture of ethylic benzylideneacetoacetate and deoxybenzoïn (1 mol.) with caustic potash (rather less than 2 mols.); if the proportion of potash used is greater than this, or if the foregoing compound is heated in alcoholic solution with a few drops of potash, 3 : 4 : 5-triphenyl-Δ_2-ketotetrahydrobenzene, melting at 186°, is produced (compare Abstr., 1893, i, 419); the *oxime* melts at 209°, whilst its *isomeride* melts at 120°.

Triphenylbenzene, [Ph_3 = 1 : 2 : 3], is formed when 3 : 4 : 5-triphenyl-Δ_2-ketotetrahydrobenzene or its isomeride is distilled with zinc chloride; it melts at 150—155° (compare A. Smith, Abstr., 1893, i, 220). Triphenylketotetrahydrobenzene yields a *bromo*-derivative, which melts at 218°, the *isomeride* melting at 175°. Potassium permanganate has no action on triphenylketotetrahydrobenzene, but is at once decolorised when the isomeric modification is warmed with it.

Condensation of ethylic benzylideneacetoacetate with deoxybenzoïn

and ammonia gives rise to *ethylic methyltriphenyldihydropyridinecarboxylate*, $CPh\langle^{CPh\cdot CHPh}_{NH-CMe}\rangle C\cdot COOEt$ (compare Paal and Strasser, Abstr., 1888, 62); it melts at 170°.

Ethylic 3-methyl-5-phenyl-Δ_2-ketotetrahydrobenzene-4 : 6-dicarboxylate (Abstr., 1893, i, 419) yields an *oxime*, which melts at 173°.

Benzylideneacetylacetone, $CAc_2{:}CHPh$, which boils at 185—188° (15 mm.), is obtained by heating the *hydrochloride* above its melting point in a vacuum, this salt being formed on leading hydrogen chloride into a well-cooled mixture of acetylacetone and benzaldehyde (1 mol.); it melts at 104—105°, hydrogen chloride being eliminated. *Benzylidenediacetylacetone*, $CHPh(CHAc_2)_2$, is produced when a few drops of diethylamine are added to a mixture of acetylacetone with benzylideneacetylacetone in molecular proportion, or by the influence of the same base on a mixture of benzaldehyde with acetylacetone (2 mols.); it melts at 166°. Hydroxylamine gives rise to a *compound* which melts at 145°, and phenylhydrazine yields a *compound* of the formula $C_{23}H_{24}N_2O_2$, melting at 177°.

3-Methyl-5-phenyl-Δ_2-ketotetrahydrobenzene, $CH\langle^{CMe\cdot CH_2}_{CO-CH_2}\rangle CHPh$, is formed on boiling benzylidenediacetylacetone with caustic potash; it melts at 35—36°, and boils at 189—194° (15—20 mm.). It is also formed when ethylic 3-methyl-5-phenyl-Δ_2-ketotetrahydrobenzene-4 : 6-dicarboxylate is boiled with caustic potash or heated with dilute hydrochloric acid at 160°. A more convenient method of preparation consists in boiling ethylic benzylidenediacetoacetate with a 10 per cent. solution of caustic potash. The *oxime* melts at 115°.

Ethylic benzylideneacetylacetoneacetoacetate is formed when a few drops of diethylamine are added to a mixture of benzylideneacetylacetone and ethylic acetoacetate (1 mol.); it melts at 156°, and is converted into the foregoing compound when boiled with dilute caustic potash. When hydrogen chloride is led through absolute alcohol in which benzylidenediacetylacetone is suspended, a *compound* is formed, which melts at 152°, and probably has the constitution

$$CH\langle^{CO\cdot CH{:}CMe}_{CMe{:}CH\cdot CO}\rangle CHPh\langle\rangle CH.$$

Deoxybenzoïnbenzylideneacetylacetone, $CHAc_2\cdot CHPh\cdot CHPh\cdot COPh$, is produced by the addition of a few drops of diethylamine to a mixture of benzylideneacetylacetone and deoxybenzoïn (1 mol.) in alcohol; it melts at 191—192°. The *oxime* melts at 205—206°.

3 : 4 : 5-Triphenyl-6-acetyl-Δ_2-ketotetrahydrobenzene,

$$CH\langle^{CPh\cdot CHPh}_{CO\cdot CHAc}\rangle CHPh,$$

melting at 221°, is formed by the action of rather less than one molecular proportion of sodium ethoxide on the foregoing ketone; the employment of two leads to the formation of 3 : 4 : 5-triphenyl-Δ_2-ketotetrahydrobenzene.

Ethylic cinnamylidenediacetoacetate, $CHPh{:}CH\cdot CH(CHAc\cdot COOEt)_2$, is obtained by the condensation of cinnamaldehyde with ethylic

acetoacetate (2 mols.) under the influence of diethylamine or piperidine (compare Biginelli, Abstr., 1890, 768). It melts at 160—161°, and if submitted to the action of hydrogen chloride, when suspended in well-cooled absolute alcohol, it gives rise to *ethylic* 3-*methyl*-5-*cinnamyl*-Δ_2-*ketotetrahydrobenzene*-4 : 6-*dicarboxylate*, which melts at 127°. Employing warm caustic soda instead of hydrogen chloride, 3-*methyl*-5-*cinnamyl*-Δ_2-*ketotetrahydrobenzene*,

$$CH\begin{matrix}\nearrow CMe\cdot CH_2\\ \searrow CO—CH_2\end{matrix}\!\!>CH\cdot CH{:}CHPh,$$

is obtained. It melts at 56° and boils at 243° (10 mm.); the *oxime* melts at 176—177°.

Ethylic methylenediacetoacetate (ethylic diacetylglutarate) is prepared by adding a small quantity of diethylamine or piperidine dissolved in alcohol to a mixture of 40 per cent. formaldehyde solution with ethylic acetoacetate (2 mols.), the liquid being well cooled for 5—6 hours. It forms a viscid oil, free from colour and odour; it boils and decomposes at 190—210° (20 mm.). Ammonia converts it into ethylic dihydrolutidinedicarboxylate (compare Griess and Harrow, Abstr., 1888, 1313). Water is eliminated from ethylic methylenediacetoacetate with formation of ethylic 3-methyl-Δ_2-ketotetrahydrobenzene-4 : 6-dicarboxylate, the latter substance yielding 3-methyl-Δ_2-ketohexenylene on hydrolysis (compare Hagemann, Abstr., 1893, i, 394). The oxime melts at 63°, and its *hydrochloride* at 159°; the *benzoyl*-derivative of the oxime forms lustrous needles which melt at 116°.

Tetrahydrometatoluidine, $CH\begin{matrix}\nearrow CMe——CH_2\\ \searrow CH(NH_2)\cdot CH_2\end{matrix}\!\!>CH_2$, is obtained by heating 3-methyl-Δ_2-ketotetrahydrobenzene with ammonium formate for five hours at 220—230°, and subsequent hydrolysis of the *formyl*-derivative, which boils at 260—275°. The free base forms a colourless liquid having an odour suggestive both of camphor and of ammonia; it boils at 152—155°, and is very volatile in a current of steam. The *hydrochloride* is readily soluble in water and alcohol, the aqueous solution decomposing when heated; the *platinochloride* melts and decomposes at 280°. The *carbamido*-derivative forms large, transparent plates which melt at 176°, and the *phenylthiocarbamido*-derivative crystallises from dilute alcohol in slender, lustrous needles which melt at 122°.

Ethylic ethylidenediacetoacetate, $CHMe(CHAc\cdot COOEt)_2$, is prepared like ethylic methylenediacetoacetate, acetaldehyde being substituted for formaldehyde; it melts at 79—80°. Ammonia converts it into ethylic dihydrocollidinedicarboxylate, whilst by the action of phenylhydrazine the *phenylhydrazide* of ethylic 3 : 5-dimethyl-6-carboxylic-Δ_2-ketotetrahydrobenzene-4-carboxylate is obtained; this is also formed by the interaction of ethylic methylenediacetoacetate and phenylhydrazine.

Ethylic 3 : 5-*dimethyl*-Δ_2-*ketotetrahydrobenzene*-4 : 6-*dicarboxylate*, $CH\begin{matrix}\nearrow CMe\cdot CH(COOEt)\\ \searrow CO\cdot CH(COOEt)\end{matrix}\!\!>CHMe$, is obtained by the elimination of 1 mol. H_2O from ethylic ethylidenediacetoacetate under the influence

of heat or dilute acids and alkalis; it is a colourless oil which boils and decomposes at 225—230° (35 mm.). The *oxime*, which melts at 175°, is obtained by the action of hydroxylamine on ethylic ethylidenediacetoacetate. Bromine gives rise to the *dibromide*, a viscid, colourless oil from which 2HBr is eliminated at 120°, yielding a *compound* which melts at 148° and boils at 258° (30 mm.); this, on hydrolysis, yields *dimethylhydroxyisophthalic acid*,

$$CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe-C(COOH)\\C(OH)\cdot C(COOH)\end{matrix}\begin{matrix}>\\<\end{matrix}CMe,$$

in minute, colourless needles, which melt and decompose at 228°, carbonic anhydride being eliminated and 1 : 3 : 5-xylenol formed.

Ethylic 3 : 5-*dimethyl*-Δ_2-*ketotetrahydrobenzene*-4-*carboxylate* is produced, together with *ethylic* 3 : 5-*dimethyl*-Δ_2-*ketotetrahydrobenzene*-6-*carboxylate*, by the hydrolysis of ethylic 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene-4 : 6-dicarboxylate; the ethylic β-carboxylate is separated from the δ-isomeride by its solubility in caustic soda.

Hydrolysis of ethylic ethylidenediacetoacetate gives rise to 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene, which yields the *oxime* melting at 166—168°, in addition to the compound described by Hantzsch (Abstr., 1883, 84), which melts at 72—74° and boils at 140—141° (19 mm.), whilst the *hydrochloride* melts at 169—170°, and the *benzoyl*-derivative at 126°. The *phenylhydrazone* of 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene melts at 76—78° and boils at 210—215° (20 mm.), whilst the *benzylidene*-derivative, having the constitution

$$CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe----CH_2\\CO\cdot C(CHPH)\end{matrix}\begin{matrix}>\\<\end{matrix}CHMe,$$

melts at 102°; the latter is identical with the benzylidene-derivative described by Sarelli (Abstr., 1893, i, 667).

The *dibromide* of 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene is a colourless, unstable oil, which is readily converted into Hantzsch's tetrabromo-derivative melting at 136°; a *bromide* melting at 86° is formed when the ketone is exposed to sunlight for 36 hours in contact with a large excess of bromine.

Tetrahydro-xylidine, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe------CH_2\\CH(NH_2)\cdot CH_2\end{matrix}\begin{matrix}>\\<\end{matrix}CHMe$, is obtained by reducing the oxime of 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene, in alcoholic solution, with sodium, or by heating the ketone with ammonium formate for five hours at 230—240°; it boils at 169—170°, and is volatile with ether vapour. The *hydrochloride* melts at 140—150°; the *platinochloride* crystallises in lustrous, orange-coloured plates, which melt and decompose at 260°; the *formyl*-derivative boils at 156—158° (18 mm.). The *carbamido*-derivative melts at 185°, and the *phenylthiocarbamido*-derivative forms long, lustrous needles, which melt at 172°. M. O. F.

Orthamidodiphenylmethane. By O. Fischer and H. Schmidt (*Ber.*, 1894, **27**, 2786—2790).—The preparation of orthamidodiphenylmethane has been previously described (Abstr., 1894, i, 200). The *sulphate*, $(C_{13}H_{13}N)_2,H_2SO_4$, crystallises in colourless needles, and

melts at 191°. The *benzoyl*-derivative crystallises in long, colourless, lustrous prisms melting at 116°. The *thiocarbamide*,

$$CS(NH\cdot C_6H_4\cdot CH_2Ph)_2,$$

is deposited in small, pale yellow crystals, and melts at 147°. *Phthalylamidodiphenylmethane*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_4\cdot CH_2Ph$, formed from phthalic anhydride and the amine, crystallises in colourless needles, and melts at 139°. *Parahydroxybenzylidenamidodiphenylmethane* and *paranitrobenzylidenamidodiphenylmethane* are formed by the interaction of the amine and parahydroxybenzaldehyde and paranitrobenzaldehyde respectively; the former is deposited in small, yellow plates melting at 110°, the latter in golden crystals melting at 105°. *Orthohydroxydiphenylmethane* and fluorene are converted into the amine by the diazo-reaction; the former is an oily liquid, volatile with steam, soluble in soda, and yielding xanthine, in small quantity, by distillation with lead oxide.

Diphenylmethaneorthazo-β-naphthol, prepared from the diazo-chloride and β-naphthol, crystallises in red needles, and melts at 134°. Two dyes are formed by the interaction of the diazo-chloride and resorcinol, they crystallise in reddish-brown needles, and can be separated by means of alcohol. The more soluble is *diphenylmethaneorthoazodihydroxybenzene*, melting at 170°; the other melts at 189°. The *sodium salts* of both are sparingly soluble.

Orthocyanodiphenylmethane, prepared from the diazo-chloride and potassium cyanide, is a pale yellow oil with a characteristic odour; it boils at 300—305° (147 mm.), and by prolonged heating with alcoholic potash is converted into *benzylbenzamide*, $CH_2Ph\cdot C_6H_4\cdot CO\cdot NH_2$, which crystallises in colourless needles, melts at 162°, and, when boiled during several days with alcoholic soda, yields benzylbenzoic acid. Anthranol is produced by the action of concentrated sulphuric acid (20 parts) at 90° on benzylbenzoic acid; its formation is probably preceded by that of anthraquinone. J. B. T.

The Benzene Nucleus. By W. Vaubel (*J. pr. Chem.*, 1894, [2], **50**, 362—366).—Auramine, amidotetramethyldiamidodiphenylmethane, reacts with four atoms of nascent bromine, instead of the two, required by the author's theory. This is probably due to the presence of the amido-group combined with the methane carbon atom. Similar behaviour is shown by other compounds. Tetramethyldiamidobenzophenone reacts with the normal number of bromine atoms, whilst the corresponding benzhydrol, in which a hydroxy-group is combined with the methane carbon atom, resembles auramine and reacts with four.

The author also replies to Knorr's criticisms (*Annalen*, 1894, **279**, 188) on his views as to the configuration of the benzene molecule, and endeavours to show, by arguments which cannot be rendered intelligible without models, that the behaviour of the phthalic acids, the constitution of pyrazole, and the etherification of aromatic acids can all be readily explained on the principles already laid down by him (Abstr., 1891, 1343). A. H.

Paradiamidodiphenylmethanesulphone. By O. STEIN (*Ber.*, 1894, **27**, 2806—2807; compare Eberhardt and Welter, Abstr., 1894, i, 451).—*Paradiamidodiphenylmethanesulphone* is the chief product of the action of fuming sulphuric acid on paradiamidodiphenylmethane, under the conditions described by the author. It crystallises from dilute ammonia in colourless, lustrous plates, melts at 217°, and becomes yellow by the prolonged action of ammonia. It gives an intense blue coloration with extremely small traces of nitrous acid, but the colour soon changes to reddish-brown, and may completely disappear after a time. No coloration is produced with diazo-compounds, and the sulphone might, therefore, be employed as an indicator in the titration of aromatic amines with sodium nitrite.

J. B. T.

Tetrahydrocarbazole. By C. U. ZANETTI and E. LEVI (*Gazzetta*, 1894, **24**, ii, 111—118).—On heating tetrahydrocarbazole with methylic iodide at 120—140° in an autoclave, and distilling the product in a current of steam, an oil is obtained, which partially dissolves in hydrochloric acid; the residue ultimately solidifies, and is found to be a mixture melting at 152—165°. If the hydrochloric acid solution, after treatment with sodium nitrite, is extracted with ether, and the ethereal solution evaporated, a *nitrosamine* is left; this, on reduction, yields a secondary base. The principal product of the action remains dissolved in the original hydrochloric acid solution, and is a base of the composition $C_{14}H_{17}N$, possibly $\begin{matrix}CH{:}CH\cdot C\cdot CH_2\cdot C\cdot CH_2\cdot CH_2\\ CH{:}CH\cdot C\cdot NMe\cdot C\cdot CH_2\cdot CH_2\end{matrix}$. It is a heavy, yellow oil, which boils at 160—165° under 14 mm. pressure, has an aromatic odour, and decomposes slowly in the air. The platinochloride, $(C_{14}H_{17}N_2)_2,H_2PtCl_6$, crystallises in lustrous, brick-red needles melting and decomposing at 204—208°.

On gradually adding chloroform to an alcoholic solution of tetrahydrocarbazole and sodium ethoxide, a *base*, $C_{13}H_{13}Cl_2N$, probably $\begin{matrix}CH{:}CH\cdot C\cdot CCl_2\cdot C\cdot CH_2\cdot CH_2\\ CH{:}CH\cdot C\cdot NH\cdot C\cdot CH_2\cdot CH_2\end{matrix}$, is formed, which may be separated from the product by decomposing its hydrochloride with alkali and extracting with ether. The base crystallises in thin, white laminæ melting at 158—159°, and has feebly basic properties; the *platinochloride* is very unstable. On heating the base with hydriodic acid and red phosphorus at 220—230°, it yields a product containing chlorine, and possessing the powerful odour of an isonitrile.

W. J. P.

Phenolphthaleïnanhydrideanilide and Galleïnanilide. By R. ALBERT (*Ber.*, 1894, **27**, 2793—2794; compare Abstr., 1894, i, 201).—*Phenolphthaleïnanhydride*, prepared by fusing a mixture of phenol, phthalic anhydride, and zinc chloride, is insoluble in alkalis, and readily forms an *anilide*, $CO<\begin{matrix}C_6H_4\\ NPh\end{matrix}>C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>O$, which crystallises in short, colourless, lustrous prisms.

Galleïnanilide, $CO<\begin{matrix}C_6H_4\\ NPh\end{matrix}>C<\begin{matrix}C_6H_2O(OH)\\ C_6H_2O(OH)\end{matrix}>O$, formed by heating galleïn with aniline (6 parts) and aniline hydrochloride (2 parts),

crystallises from alcohol or glacial acetic acid in colourless, lustrous plates, and melts above 300°. The *dimethylic ether* crystallises in slender, colourless needles, and melts at 205°. J. B. T.

Fluoresceïnanilides. By O. Fischer and E. Hepp (*Ber.*, 1894, **27**, 2790—2793; compare Abstr., 1893, i, 721, and preceding abstract).—The phthaleïns are divisible into three groups. The term *leucophthaleïns* is applied to those which, together with their simpler derivatives, are colourless, and are probably represented by Baeyer's phthaleïn formula. The coloured phthaleïns, which also yield coloured salts, ethers, and simple substitution products, are termed *quinoidal phthaleïns;* fluoresceïn and galleïn belong to this class. *Tautophthaleïns* are those which are colourless but yield coloured salts, such as phenolphthaleïn, paradiamidophthalophenone, and orcinolphthaleïn.

Fluoresceïnanilide dimethylic ether is not hydrolysed by boiling with dilute alcoholic sulphuric acid, but is by the action of hydrochloric acid at 150°; *fluoresceïn dimethylic ether* is formed, and crystallises in slender, colourless needles, melting at 198°. It gives a red coloration, in alcoholic solution, with mineral acids, and dissolves in concentrated sulphuric acid with a green fluorescence. *Fluoresceïnanilide diethylic ether* crystallises in colourless prisms, melts at 162—164°, loses alcohol of crystallisation by prolonged boiling at 120°, and gives a green fluorescence with concentrated sulphuric acid. By the prolonged action of concentrated acids, fluoresceïnanilide diethylic ether is hydrolysed, aniline, alcohol, fluoresceïn, and *isofluoresceïn diethylic ether*, $CO<^{C_6H_4}_{O}>C<^{C_6H_3(OEt)}_{C_6H_3(OEt)}>O$, being formed; the last, after repeated crystallisation from benzene and ether, is deposited in colourless, tetragonal prisms, becomes yellow, and melts at 181—182°. With sulphuric acid, it gives a yellow solution with green fluorescence. In alcoholic solution, mineral acids give a red coloration. Baeyer's fluoresceïn diethylic ether is yellow, and is probably the quinoidal form. Attempts to prepare colourless fluoresceïn from either of the ethers were unsuccessful.

Phthalophenoneanilide, $CO<^{C_6H_4}_{NPh}>CPh_2$, prepared from phthalophenone, aniline, and aniline hydrochloride, crystallises in vitreous prisms, melts at 189°, dissolves without coloration in concentrated sulphuric acid, and is precipitated on dilution. It is resolved into its constituents by the action of concentrated hydrochloric acid at 180°, but with alcoholic sulphuric acid (30 per cent.), at the same temperature, the larger part remains unchanged even after eight hours' heating. J. B. T.

Action of Nascent Bromine on the Triphenylmethane Colouring Matters. By W. Vaubel (*J. pr. Chem.*, 1894, [2], **50**, 347—351; compare Abstr., 1893, i, 360).—Nascent bromine acts on the amidotriphenylmethane colouring matters in accordance with the rules already established by the author, that the amido- and monalkylamido-groups favour the introduction of bromine into the para- and the two ortho-positions, whilst the dialkylamido-group only permits its entrance into the para- and one ortho-position. This must, how-

cver, be slightly modified when applied to these dyes, since the characteristic mode of combination of one of the nitrogen atoms in some instances seems to affect the number of atoms of bromine which can be taken up.

The action, in most cases, proceeds quantitatively, and may be employed for the determination of the amount of colouring matter present. Tetramethyldiamidotriphenylmethane, "brilliant-green," and "methyl-green" react with two atoms of bromine; hexamethylpararosaniline and "crystal-violet" require three atoms, rosaniline four, and leucaniline and pararosaniline five atoms. Aurin and phenolphthaleïn both require four atoms of bromine, this being in accordance with the previous conclusions drawn by the author from his former experiments on hydroxy-compounds. A. H.

The Triphenylmethane Colouring Matters. By W. VAUBEL (*J. pr. Chem.*, 1894, [2], **50**, 351—361; compare preceding abstract).—The fact that leucaniline reacts with five atoms of nascent bromine, whilst rosaniline only reacts with four, shows that the number of atoms of bromine taken up by the molecule is influenced by the mode of combination of one of the nitrogen atoms in rosaniline, and the author considers that only the formula of E. and O. Fischer can explain this phenomenon. He further shows that if the total number of atoms of bromine which can be introduced into the molecule of a colouring matter by treating it with nascent bromine, be taken as a measure of the total basicity of the amido-groups of the compound, it will be found that as the basicity increases the colour of the substance passes from green through blue and bluish-violet to violet and reddish-violet. A. H.

Halogen-additive Compounds from α- and β-Naphthaquinone. By T. ZINCKE and M. SCHMIDT (*Ber.*, 1894, **27**, 2753—2762).—*α-Naphthaquinone dichloride*, $C_6H_4<\begin{matrix}CO\cdot CHCl\\ CO\cdot CHCl\end{matrix}$, is obtained by the direct action of chlorine on α-naphthaquinone in acetic acid solution. It is very sparingly soluble in alcohol, and crystallises from benzene in colourless prisms, which melt and decompose at 176°. The dichloride is not affected by the continued action of chlorine or bromine, or of bleaching powder solution, but is slowly converted into chlorhydroxynaphthaquinone by alkalis. It readily loses hydrogen chloride, forming the chloro-α-naphthaquinone which melts at 117°; chlorine converts the latter into dichloronaphthaquinone, which can readily be prepared in this way.

α-Naphthaquinone dibromide forms broad, colourless tablets or plates, melts and decomposes at 92°, and resembles the chloride in its chemical properties. *Brom-α-naphthaquinone*, prepared by boiling the bromide with acetic acid and sodium acetate, forms small, compact crystals melting at 130°.

β-Naphthaquinone dichloride, $C_6H_4<\begin{matrix}CO-CO\\ CHCl\cdot CHCl\end{matrix} + 2H_2O$, crystallises in white plates or broad needles, and melts at 86°. It readily loses hydrogen chloride, and is slowly converted by bleaching-powder

solution into the lactone of dichloro-β-hydroxyorthocarboxyhydrocinnamic acid, $CO<^{-O-}_{C_5H_4}>CH\cdot CCl_2\cdot COOH$ (Abstr., 1894, i, 289), chloro-β-naphthaquinone being probably formed as an intermediate product.

Aqueous sulphurous acid converts the dichloride into monochloro-β-naphthaquinol (Abstr., 1887, 53), which yields a *diacetate* melting at 149°.

When treated with aqueous soda, the dichloride is partially converted into chlorhydroxynaphthaquinone, and partially into *chlororthovinylbenzoylcarboxylic acid*, $COOH\cdot CO\cdot C_6H_4\cdot C_2H_2Cl$, which crystallises in yellow needles, and melts at 102—103°. On oxidation, this acid yields *chlororthovinylbenzoic acid*, $COOH\cdot C_6H_4\cdot CH{:}CHCl$, which crystallises in scales, melts at 151—152°, and is converted by reduction into orthoethylbenzoic acid.

β-Naphthaquinone dibromide forms small, yellow crystals, and melts and decomposes at 65°. It rapidly decomposes when kept, and loses hydrogen bromide when dissolved in alcohol. A. H.

Tetrahydronaphthalic acid. By C. Zengelis (*Ber.*, 1894, **27**, 2694—2695).—When dihydronaphthalic acid (Anselm, Abstr., 1889, 717) is heated at 140° with hydriodic acid and phosphorus, it is further reduced to *tetrahydronaphthalic acid*, $C_{10}H_{10}(COOH)_2$. This has no definite melting point, but at 185° begins to be converted into the *anhydride*, which melts at 119·5°, and dissolves in alkalis. The acid yields a *monethylic salt* melting at 48°, and also nitro-derivatives. Heating with sulphuric acid converts it into naphthalic anhydride.

C. F. B.

Orthodiamines. By O. Fischer (*Ber.*, 1894, **27**, 2773—2781; compare Abstr., 1893, i, 283).—*β-Phenylnaphthylene carbamide*,

$$C_{10}H_6<^{NH}_{NPh}>CO,$$

prepared from carbonyl chloride and β-phenyl-1 : 2-naphthylenediamine, crystallises in long, colourless prisms, melts at 238°, and exhibits a blue fluorescence in benzene solution. The stability of the compound towards acids and alkalis is in favour of the formula given above, but opposed to the alternative formula

$$CO{:}N\cdot C_{10}H_6\cdot NHPh.$$

n-Phenylnaphthimidazole-β-phenylorthocarboxylic acid,

$$C_{10}H_6<^{-N}_{NPh}>C\cdot C_6H_4\cdot COOH,$$

obtained by the interaction of the diamine and phthalic anhydride, crystallises in colourless prisms, melts at 260°, and forms salts with both acids and bases. The *calcium* salt crystallises in stellate needles; the *picrate* is deposited in pale yellow prisms, and explodes at 260°. The *hydrochloride*, $C_{24}H_{16}N_2O_2,HCl$, crystallises in lustrous needles.

n-Phenylnaphthimidazole-β-propionic acid,

$$C_{10}H_6<^{-N}_{NPh}>C\cdot CH_2\cdot CH_2\cdot COOH,$$

is formed by heating the diamine with succinic anhydride; it crystallises in reddish plates, melts at 180—181°, shows a blue fluorescence in benzene solution, and has both basic and acidic properties. The *hydrochloride* crystallises from alcohol in colourless needles, from hydrochloric acid in long prisms, and is dissociated by water. The *picrate* forms long yellow needles; the *silver salt* is colourless, pulverulent, and stable towards light.

The preparation of α-ethyl-β-phenylnaphthylenediamine has been previously described; the red dye which is formed as a bye-product, dissolves in concentrated sulphuric acid with a blue coloration, and is probably an oxidation product of phenylnaphthylenediamine. The *hydrobromide* crystallises in lustrous, bronze plates.

α-Ethyl-β-phenylnaphthylenethiocarbamide, $C_{10}H_6<^{NEt}_{NPh}>CS$, formed by the action of carbon bisulphide on the diamine, is very sparingly soluble, crystallises in short, colourless prisms, and melts above 300°.

By the action of formic acid and zinc chloride, of chloral, or of commercial formaldehyde on the diamine, a *naphthimidazol derivative*, $C_{10}H_6<^{NEt}_{NPh}>CH\cdot OH$, is formed; it crystallises in colourless needles, melts at 161°, and its solutions fluoresce like petroleum; a fugitive blue coloration is obtained with concentrated sulphuric acid. The compound is stable towards acids and alkalis. The diamine reacts in the ordinary manner with acetic anhydride, and although the formation of the imidazol from formic acid is easily understood, its preparation from formaldehyde, which was almost free from acid, is difficult to explain. The *platinochloride*, $(C_{19}H_{18}N_2O)_2,H_2PtCl_6$, crystallises in brownish-yellow needles, and dissociates in contact with water.

Paratolylnaphthylenediamine has been previously described (Abstr., 1892, 1472); it melts at 146—147°. The *hydrochloride* crystallises in needles. On oxidation with lead oxide, the base yields a tolunaphthazine, $C_{10}H_6<^{N}_{N}>C_6H_4Me$, which has been previously prepared by Witt (Abstr., 1887, 591).

n-Paratolylnaphthimidazole, formed by the interaction of the diamine and formaldehyde, crystallises in colourless prisms, and melts at about 200°. *Symmetrical ethylparatolyl-1 : 2-naphthylenediamine*, $NHEt\cdot C_{10}H_6\cdot NHPh$, obtained by the action of ethylic bromide on the diamine, crystallises in flat, colourless, lustrous needles, and melts at 68°. That it is a secondary base is shown by the formation of a *mononitrosamine*, which crystallises in yellow plates, and melts at 138°.

1 : *n-Ethyl-2 : n-paratolyldihydronaphthimidazole*,

$$C_{10}H_6<^{NEt\text{——}}_{N(C_7H_7)}>CH_2,$$

prepared from formaldehyde and the diamine, crystallises in colourless prisms, and melts at 175—178°. The compound is extremely stable, and is not acted on by dilute sulphuric acid at 150°; its solutions exhibit a blue fluorescence. *1-Benzyl-2-tolylnaphthylenediamine* is formed by the interaction of benzylic chloride and paratolyl-1 : 2-

naphthylenediamine; it crystallises from alcohol in pale yellow prisms, and melts at 157°. The *hydrochloride* crystallises in colourless, lustrous plates, melts at 204°, and its solutions, like those of the base, exhibit a blue fluorescence. The *acetyl derivative* is deposited from alcohol in colourless plates melting at 162°. 1 : *n-Benzyl*-2 : *n-tolyldihydronaphthimidazole*, formed by the action of formaldehyde on the base, crystallises from alcohol in colourless prisms, and melts at 125°.

The anhydro-base (m. p. 165—166°), previously obtained (*loc. cit.*) from benzaldehyde and orthamidoparaditolylamine, is also formed from benzoic chloride and orthamidoditolylamine. The *carboxylic acid*, $C_6H_3Me<\overset{N(C_7H_7)}{\underset{\quad N}{\quad}}>C\cdot C_6H_4\cdot COOH$ [$NC_7H_7 : N : Me = 1 : 2 : 4$], is prepared by heating phthalic anhydride with amidoditolylamine; it crystallises in colourless needles, melts at 173°, dissolves in alkalis, and is precipitated by acids. The acid,

$$C_6H_3Me<\overset{N(C_7H_7)}{\underset{\quad N}{\quad}}>C\cdot C_2H_4\cdot COOH,$$

formed in a similar manner from succinic anhydride and the amine, crystallises in slender, colourless needles melting at 228°.

Orthamidoditolylamine, when oxidised with lead oxide, yields a *ditolazine*, $C_6H_3Me<\overset{N}{\underset{N}{<}}>C_6H_3Me$ [Me : N : N = 1 : 3 : 4; 1 : 3 : 4 or 1 : 3 : 4; 1 : 4 : 5]; the reaction is similar to the formation of phenazine from orthamidodiphenylamine. The compound crystallises in pale yellow needles, melts at 156°, and, with sulphuric acid, gives a blood-red coloration, changing to yellow when diluted.

J. B. T.

Terpenes and Ethereal Oils. By O. Wallach (*Annalen*, 1894, **281**, 127—147 and 147—166; compare Abstr., 1891, 1240).—When limonene tetrabromide is warmed on the water bath with a solution of sodium in methylic alcohol, a *compound* is obtained which has the constitution $C_{10}H_{14}Br\cdot OMe$; it boils at 137—140° (14 mm.); the sp. gr. = 1·251 at 18°, and n_D = 1·51963 at the same temperature. When treated with hydrogen bromide in glacial acetic acid, it yields dipentene tetrabromide, and the action of sodium ethoxide gives rise to *carveol methyl ether*, $C_{10}H_{15}\cdot OMe$, an oil of pleasant odour, which boils at 210—212°, has a sp. gr. = 0·9065 at 18°, and a specific refractive index n_D = 1·47586 at this temperature. On oxidation with chromic anhydride in glacial acetic acid solution, carveol methyl ether yields carvone, the transformation of limonene into carvone being thus effected. Terpineol also may be converted into carvone in a similar manner, since the tetrabromide yields carveol methyl ether by the action of sodium methoxide. Cymene is formed when terpineol tribromide is boiled with alcoholic potassium cyanide.

The author cannot confirm his former conclusion, that the dipentene dihydriodides described by him correspond with v. Baeyer's dihydrobromides and dihydrochlorides. The sole product of the action of phosphorus triiodide on terpin hydrate is the hydriodide, $C_{10}H_{18}I_2$, which melts at 70°.

Pinole dibromide is converted into cymene by energetic reducing agents, such as formic acid or zinc-dust and glacial acetic acid; the latter also gives rise to the diacetate of pinole glycol when boiled, whilst under other conditions solid terpineol is formed.

Pinole tribromide, $C_{10}H_{17}OBr_3$ (compare Abstr., 1891, 218), is most conveniently prepared by treating pinole dibromide with hydrogen bromide in glacial acetic acid. When reduced in alcoholic solution with sodium, it yields a *compound* which boils at 225°; the *oxime* melts at 82—83°. If reduction is effected by means of zinc-dust and glacial acetic acid, an unsaturated *ketone*, $C_{10}H_{16}O$, is formed, boiling at 213—218°; the *secondary alcohol*, $C_{10}H_{18}O$, derived from this substance, boils at 218—220°, and has the specific rotatory power $n_D = 1{\cdot}47096$ at 21°, and the sp. gr. = 0·91 at the same temperature. The alcohol is very viscous, and has a pleasant odour resembling that of linaloöl and terpineol; the ketone is regenerated from it by oxidation.

The author discusses the constitution of pinole, representing it by the formula $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CMe{\cdot}CH\\CH_2{\cdot}CPr\end{matrix}\begin{matrix}>\\>\end{matrix}\begin{matrix}CH_2\\\end{matrix}\Big\rangle O$. M. O. F.

Combination of Borneol, Camphor, and Monochlorcamphor with Aluminium Chloride. By G. Perrier (*Compt. rend.*, 1894, **119**, 276—277).—When powdered borneol (2 mols.) is heated with anhydrous aluminium chloride (1 mol.) at about 70—80°, an energetic action takes place without liberation of hydrogen chloride, and the mixture partially liquefies. If the reaction is completed by heating at 110—120°, a homogeneous liquid is obtained which, on cooling, solidifies to a brownish-yellow crystalline mass. In presence of a small quantity of carbon bisulphide, the reaction takes place at the ordinary temperature, and a well-defined product is obtained in bulky crystals, but if a large proportion of the bisulphide is used, the yield is much lower. The product, which has the composition $(C_{10}H_{18}O)_2,Al_2Cl_6$, alters readily on exposure to air, and becomes rose-coloured by the action of light. Water decomposes it somewhat rapidly with separation of borneol and production of a solution of aluminium chloride. Hot benzene, toluene, and chloroform partially decompose it with liberation of hydrogen chloride.

Camphor, under the same conditions, yields an analogous compound, $(C_{10}H_{16}O)_2,Al_2Cl_6$, which crystallises in plates. It becomes red when exposed to light, and alters rapidly when exposed to air. It is decomposed by water with liberation of camphor. Monochlorocamphor, melting at 97°, also yields a product analogous in composition and properties.

Ferric chloride likewise combines with borneol, camphor, and monochlorocamphor, but the products have not yet been analysed. C. H. B.

Nitrocamphor. By N. Tarugi (*Gazzetta*, 1894, **24**, i, 528—531).—On reducing β-nitrocamphor melting at 83° with sodium in alcoholic solution, a *sodium* salt which is very soluble in water, but practically insoluble in concentrated soda, is obtained; it yields a yellow floccu-

lent *substance* on treatment with hydrochloric acid. This, when heated with acetic acid, is converted into α-nitrocamphor, melting at 102—103°. W. J. P.

Action of Nitrous acid on Amidocamphor. By A. Angeli (*Gazzetta*, 1894, **24**, ii, 44—52).—Monoketoazocamphoquinone, $C_8H_{14}<\begin{matrix}CN_2\\CO\end{matrix}$ (Abstr., 1893, i, 570), behaves like a diazo-compound; on heating, it evolves nitrogen, leaving camphenone and azocamphanone.

Camphenone, $C_{10}H_{13}{\cdot}CO$, separates from petroleum in colourless crystals melting at 168—170°; its *oxime*, $C_{10}H_{14}{\cdot}NOH$, crystallises in magnificent colourless plates melting at 132°.

Azocamphanone,

$$C_8H_{14}<\begin{matrix}C{\cdot}N{\cdot}N{\cdot}C\\CO\quad\quad OC\end{matrix}>C_8H_{14} \text{ or } C_8H_{13}<\begin{matrix}CH{\cdot}N{\cdot}N{\cdot}CH\\CO\quad\quad\quad CO\end{matrix}>C_8H_{13}\,(?),$$

crystallises in lustrous scales melting at 222°. W. J. P.

Isocampholic acid. By Guerbet (*Compt. rend.*, 1894, **119**, 278—280).—The residue from the preparation of campholic acid by the author's method of heating camphor, sodiocamphor, and sodioborneol in sealed tubes, contains another acid, *isocampholic acid*, which has the same composition.

The campholic acid is liberated by passing a current of carbonic anhydride through the faintly alkaline liquid, and the isocampholic acid is precipitated on adding hydrochloric acid. In order to purify it, it is dissolved in ether, dried over calcium chloride, the ether distilled off, and the residue mixed with its own weight of absolute alcohol and saturated with hydrogen chloride at 0°. Under these conditions, isocampholic acid yields an alkyl salt, whilst campholic acid does not. After remaining for 12 hours at the ordinary temperature, the liquid is treated with a large quantity of water, and the oily, supernatant liquid is decanted off, and washed with dilute sodium hydroxide solution to remove campholic acid. The ethylic isocampholate is dried over calcium chloride and fractionated. The portion boiling between 215° and 240° is hydrolysed by means of alcoholic potash, and the acid is converted into the calcium salt, which is purified by repeated crystallisations from absolute alcohol. It is then again converted into the ethylic salt, the fraction which boils between 228—229° is hydrolysed, and the free acid dried and distilled under reduced pressure.

Isocampholic acid, $C_{10}H_{18}O_2$, boils at 180—181°, under a pressure of 65 mm., and at 256—257° with partial decomposition under ordinary pressure; sp. gr. at 0° = 0·9941; rotatory power, $[\alpha]_D$ = + 24° 38′; vapour density = 4·90 (Cal. 5·88). The vapour density of the methylic salt, however, is 6·43 (Cal. 6·37), and of the ethylic salt 6·85 (Cal. 6 85). The acid is a colourless, oily liquid, with a disagreeable odour recalling that of valeric acid. It is almost insoluble in water, but is miscible with alcohol and ether. It does not

combine with bromine, and its salts crystallise readily from water, alcohol, or ether.

Methylic isocampholate is a colourless, oily liquid boiling at 216—218°; sp. gr. at 0° = 0·9593. The *ethylic* salt is a colourless, oily liquid with a very disagreeable odour; sp. gr. at 0° = 0·9477.

Isocampholamide, obtained by heating the ammonium salt at 210° for six hours, crystallises from boiling water in nacreous plates, which are almost insoluble in cold water. It melts at 116°, and dissolves very readily in alcohol and in ether. C. H. B.

Hydroxymethylene Compounds. By L. Claisen (*Annalen*, 1894, **281**, 306—313; compare next abstract and Abstr., 1893, i, 360, 480).—The formyl ketones are unstable substances, three molecules readily condensing to form a benzene derivative (Abstr., 1890, 357). They have the general formula $R{\cdot}CO{\cdot}CH_2{\cdot}COH$, and homologues of them having the constitution $R{\cdot}CO{\cdot}CHR{\cdot}COH$, can easily be prepared. The behaviour of the formyl ketones towards ferric chloride may be used as a method of distinguishing between ketones containing the group -COMe or $-CO{\cdot}CH_2R$ and those containing the group $-CO{\cdot}CHR_2$ or $-CO{\cdot}CR_3$. The ketone, in ethereal solution, is treated with ethylic formate and sodium, the excess of sodium removed by adding alcohol, the solution acidified with acetic acid, and water added; the ethereal solution, when diluted with alcohol and treated with ferric chloride, turns red if a ketone of a primary acid is present, but only gives dull brownish-yellow colours with the ketones of secondary or tertiary acids. Acetone and its normal homologues, ethylic levulinate, mesitylic oxide, acetophenone, benzylideneacetone, and others, give the red colour; phenyl isopropyl ketone, benzophenone, phorone, and dibenzylideneacetone give feeble brown solutions readily distinguished from the former. W. J. P.

Hydroxymethylenecamphor. By A. W. Bishop, L. Claisen, and W. Sinclair (*Annalen*, 1894, **281**, 314—398; compare Abstr., 1893, i, 360, 480).—Hydroxymethylenecamphor or camphoraldehyde, $C_8H_{14}<\begin{matrix}C{:}CH{\cdot}OH\\ |\\ CO\end{matrix}$ (compare Abstr., 1889, 619), crystallises in small, colourless prisms melting at 80—81°; it is very sparingly soluble in cold water, giving a solution which reddens litmus. It slowly and spontaneously changes to an amorphous, pasty mass, which is converted into the crystalline modification on distillation in a current of steam. It is soluble in soda, and only partially and slowly precipitated from the solution by carbonic anhydride. The *ammonium* and *potassium* salts were prepared, and also a *copper* salt of the composition $(C_{11}H_{15}O_2)_2Cu,2C_{11}H_{16}O_2$, which crystallises in silky needles melting at 126°. The *ferric* salt, $(C_{11}H_{15}O_2)_3Fe$, crystallises in dark violet leaflets, and partially sublimes when heated in a vacuum; it converts potassium cyanide into ferrocyanide in dilute alcoholic solution. Although the salt is insoluble in water, yet, after adding ferric chloride to its alcoholic solution, the latter is no longer precipitated by water; in place of a salt of the composition FeR_3, one of

the composition $FeRCl_2$ or FeR_2Cl is probably formed, although it could not be isolated.

Hydroxymethylenecamphor yields camphor and sodium formate on hydrolysis with soda, bromocamphor melting at 75—76° on treatment with bromine, and camphoric acid on oxidation with alkaline permanganate; when oxidised with chromic acid, it gives camphororthoquinone. On adding diazobenzene chloride to its soda solution, camphoquinonemonophenylhydrazone separates; hydroxylamine hydrochloride acts on the soda solution yielding a colourless viscous liquid which slowly turns brown and blue, and is probably either formylcamphoroxime or hydroxymethylenecamphorhydroxylamide. If the hydroxylamine is added to the heated solution, cyanocamphor is obtained; this process should be a very convenient one for preparing the latter substance.

Hydroxymethylenecamphorphenylpyrazole, $C_8H_{14}<\begin{matrix}C-CH\\ \|\\ C\cdot NPh\end{matrix}>N$, is prepared by warming hydroxymethylenecamphor with phenylhydrazine in acetic acid solution; it crystallises in monosymmetric plates or prisms, melting at 124—125°; $a : b : c = 1{\cdot}8956 : 1 : 1{\cdot}3478$. $\beta = 115° 43'$.

Amidomethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}NH_2$, is obtained by treating the hydroxy-derivative with ammonia; it crystallises in colourless, lustrous leaflets melting at 164—165°. It dissolves completely in dilute hydrochloric acid, but the solution immediately deposits a mixture of hydroxymethylenecamphor and *imidomethylenecamphor*, $NH(CH{:}C_{10}H_4O)_2$. The latter is most conveniently prepared by melting amido- and hydroxy-methylenecamphor together, and is also formed by heating chloromethylenecamphor with excess of methylic-alcoholic ammonia at 100°; it crystallises in minute cubes melting at 220—221°.

Anilidomethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}NHPh$, crystallises in lustrous prisms melting at 167—170°; it may be prepared by heating ethoxymethylenecamphor or chloromethylenecamphor with aniline. The corresponding *paratoluido*-derivative crystallises in thin prisms melting at 188—189°. *Methylanilidomethylenecamphor*,

$$C_{10}H_{14}O{:}CH{\cdot}NMePh,$$

crystallises in lustrous orthorhombic prisms melting at 124°; $a : b : c = 0{\cdot}792 : 1 : 0{\cdot}7535$.

Chloromethylenecamphor, $C_{10}H_{14}O{:}CHCl$, prepared by the action of phosphorus trichloride on hydroxymethylenecamphor, is a colourless oil of camphor-like odour; it has a sp. gr. of 1·09 at 15°, boils at 241—242°, and melts at 11—12°. It is accompanied by *hydroxymethylenecamphor hydrogen phosphite*, $C_{10}H_{14}O{:}CH{\cdot}O{\cdot}P(OH)_2$, which crystallises in colourless needles melting at 113—115°. *Bromomethylenecamphor* crystallises in long needles melting at 31—32°, and boils at 260—261°.

On heating the potassium derivative of hydroxymethylenecamphor, an *anhydride*, $(C_{10}H_{14}O{:}CH)_2O$, is obtained; it crystallises in lustrous monosymmetric plates melting at 188—189°; $a : b : c =$

1·9105 : 1 : 1·8011. $\beta = 96° 35·5'$. It boils without decomposition, and is readily hydrolysed by alcoholic potash.

The alkylic derivatives of hydroxymethylenecamphor are readily obtained by the usual methods; the following have been prepared.

Methoxymethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}OMe$, crystallises in prisms melting at 40°; it boils at 262°. The corresponding *ethoxy*-compound is a colourless oil boiling at 269—270°, and having a sp. gr. = 1·007 at 15°. The *benzyloxy*-derivative forms a colourless crystalline mass melting at 45—46°, and boiling at 222—224° under 15 mm. pressure. The *phenoxy*-derivative is a colourless, viscid oil which boils at 320° undergoing slight decomposition. These substances are readily hydrolysed by fuming hydrobromic acid in the cold, showing that they are true alkyloxy-derivatives.

Acetoxymethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}OAc$, melts at 63—64°, and boils at 290—293°; on prolonged heating with alcoholic sodium ethoxide, it yields the hydroxy-derivative.

Two, probably stereoisomeric, benzoyl-derivatives of hydroxymethylenecamphor can be prepared. *α-Benzoxymethylenecamphor*,

$$C_{10}H_{14}O{:}CH{\cdot}OBz,$$

is obtained by heating benzoic chloride with hydroxymethylenecamphor at 140—160°; by warming an alcoholic solution of the latter with sodium ethoxide and benzoic chloride; by the action of benzoic chloride on the sodio-derivative of the hydroxy-compound suspended in ether; or by adding benzoic chloride to a soda solution of the hydroxy-compound. It crystallises in six-sided orthorhombic plates melting at 119—120°, and boils without much decomposition at 370°; $a : b : c = 0·5767 : 1 : 1·3814$. *β-Benzoxymethylenecamphor* is obtained together with the α-modification by the action of benzoic chloride on sodium ethoxide and the hydroxy-compound in ethereal solution at − 15°; it crystallises in large, lustrous monosymmetric crystals melting at 91—92°; $a : b : c = 1·0679 : 1 : 0·9946$. $\beta = 119° 8'$. The α-isomeride has the specific rotations $[\alpha]_D = + 139·02°$ and 140·68° in 4·5 and 13·5 per cent. benzene solutions at 20°; under similar conditions, the β-modification has the specific rotations $[\alpha]_D = + 159·3°$ and 161·9°. The β-modification is converted into the α-form by heating its alcoholic solution with a little hydrochloric acid, or by distilling it; the β-modification cannot be converted into the α-isomeride. Both forms give the same hydroxymethylenecamphor when heated with alkalis. If, during the preparation of the benzoyl-derivative in alcoholic sodium ethoxide solution, the temperature be allowed to rise, ethylic benzoate is produced.

Cyanomethylenecamphor, $C_{10}H_{14}O{:}CH{\cdot}CN$, is prepared by treating the chloro- or hydroxy-derivative with potassium cyanide in methylic alcohol solution; it forms a crystalline mass melting at 46—47° and boiling at 279—282°. In the action of potassium cyanide or hydrocyanic acid on hydroxymethylenecamphor, the *cyanhydrin*,

$$C_8H_{11}<\begin{matrix}CH{\cdot}CH(CN){\cdot}OH\\ |\\ CO\end{matrix},$$

of the latter is formed; it crystallises in silky needles melting at 122—123°, has a feebly acid reaction, and is converted into the cyano-derivative on heating with acetic anhydride.

Methylenecamphorcarboxylic acid, $C_{10}H_{14}O{:}CH{\cdot}COOH$, is obtained by hydrolysing the cyano-derivative with hydrochloric acid; it crystallises in compact prisms melting at 100—102°, distils and slightly carbonises at 320°, and is soluble in hot water. The *silver* salt is a white powder, and the *methylic* salt melts at 62—63°. The acid yields a *compound*, $C_8H_{14}<\begin{matrix}C{\cdot}CO{\cdot}O{\cdot}C\\ \|\\ C{\cdot}O{\cdot}CO{\cdot}C\end{matrix}>C_8H_{14}$ (?), on heating with acetic chloride; this substance has the normal molecular weight in boiling benzene or nitrobenzene solution, and crystallises in small, colourless needles melting at 195—196°.

Hydroxymethylenementhone, $C_8H_{16}<\begin{matrix}C{:}CH{\cdot}OH\\ |\\ CO\end{matrix}$, is prepared by the action of sodium and amylic formate on an ethereal solution of menthone; it is a colourless oil of agreeable odour boiling at 250—252°, and having a sp. gr. = 1·002 at 15°. The *sodio*-derivative crystallises in colourless leaflets or prisms. It is very readily hydrolysed in alkaline solutions yielding menthone and formic acid.

Acetoxymethylenementhone, $C_{10}H_{16}O{:}CH{\cdot}OAc$, is a colourless oil boiling at 160—162° under 12—13 mm. pressure. The *benzoxy*-derivative crystallises in white leaflets melting at 75—76°. The *methoxy*-derivative (?), which boils at 250—260°, is formed together with *methylmenthone*, $C_{10}H_{17}MeO$, boiling at 213—215°, by the action of methylic iodide and sodium methoxide on hydroxymethylenementhone.

An improved method for preparing hydroxymethylenepropyl phenyl ketone is given; it melts at 87—89°, and boils at 260—262° with slight decomposition. The *acetoxy*-derivative, $COPh{\cdot}CEt{:}CH{\cdot}OAc$, is a colourless oil boiling at 167—168° under 13 mm. pressure. The *methylanilide*, $COPh{\cdot}CEt{:}CH{\cdot}NMePh$, crystallises in white needles melting at 72—73°.

Methylic hydroxymethylenephenylacetate is a colourless, viscous oil boiling at 135—136° under 14 mm. pressure. The *acetoxy*-derivative, $CPh(COOMe){:}CH{\cdot}OAc$, is an oil boiling at 176° under 16—17 mm. pressure. W. J. P.

Digitogenin Derivatives. By H. Kiliani and M. Bazlen (*Arch. Pharm.*, 1894, **232**, 334—345; compare Abstr., 1893, i, 665).—Digitogenic acid is prepared from digitogenin by treating it with glacial acetic acid (10 parts) and subsequently oxidising with chromic anhydride (0·7 part) dissolved in water (1·4 parts). After further dilution with water (10 parts), the acid is extracted by means of ether. This method is less costly and troublesome than the one formerly described, and the yield is the same. *Digitogenic acid oxime*, $C_{14}H_{21}O_3N$, crystallises in needles or prisms, melts at 175°, has an acid reaction, and dissolves in sodium carbonate with evolution of carbonic anhydride. The *magnesium salt* $(C_{14}H_{20}O_3N)_2Mg$ and the *barium salt* are crystalline, the latter being deposited in needles.

Attempts to prepare ethereal salts of digitic acid and acetyl-β-anhydrodigitic acid (see below) were unsuccessful; *ethylic digitoate* crystallises in needles or prisms, commences to soften at 120°, and melts at about 160°. Attempts to prepare isopyrocamphenic acid, for comparison with the author's bibasic acid $C_9H_{10}O_4$ (*loc. cit.*), failed; the latter compound is readily oxidised when heated with potassium permanganate; by the action of more concentrated potassium permanganate solution at ordinary temperatures, *digic acid*, $C_8H_{12}O_3$, is formed; this is deposited in granules, and softens at about 130°. The *calcium salt* $(C_8H_{11}O_2)_2Ca + 6H_2O$, crystallises in needles or prisms; the anhydrous salt is extremely hygroscopic. The *barium salt* is also crystalline. *α-Anhydrodigitic acid*, $C_{10}H_{14}O_3$, is obtained by the action, at low temperatures, of hydrogen chloride in glacial acetic acid solution on digitic acid; it melts and decomposes at about 245°, gives a red coloration changing to greenish-yellow with concentrated sulphuric acid, and readily decolorises potassium permanganate solution, digitic acid being regenerated. The acid forms an additive compound with bromine, and gives with hydrogen iodide in glacial acetic acid solution, an iodine derivative, which combines with aniline; the resulting compound contains nitrogen and, in glacial acetic acid solution, gives a violet-red dye on exposure to the air. The alkali salts yield amorphous precipitates with calcium chloride; the *potassium salt*, when treated successively with alcohol and calcium chloride, forms a crystalline compound, which decomposes when dry. *Acetyl-β-anhydrodigitic acid*, $C_{10}H_{13}O_3Ac + H_2O$, is prepared by the action of hydrogen chloride on α-anhydrodigitic acid in presence of glacial acetic acid and acetic anhydride; it crystallises in needles or prisms, softens at 140°, and melts at 170°; it reacts with sulphuric acid like α-anhydrodigitic acid. *β-Anhydrodigitic acid* is prepared from the preceding compound by hydrolysing it with potash; it crystallises in long, lustrous, colourless needles, melts and decomposes at 262—263°, and turns yellow on exposure to light and air. The *silver salt* was prepared. The formation of acetyl-β-anhydrodigitic acid probably depends on the production of acetic chloride from the acetic anhydride and hydrogen chloride, and points to the existence of the group C·O·C in α-anhydrodigitic acid, and presumably, also, in digitic acid. J. B. T.

Presence of Several Distinct Chlorophylls in the Same Vegetable Species. By A. Étard (*Compt. rend.*, 1894, **119**, 289—291).—Amongst the products of the extraction of leaves by carbon bisulphide are monohydric and polyhydric alcohols of high molecular weight, which retain chlorophyll with great tenacity, and can be repeatedly crystallised from acetic acid and other solvents without losing their colour. According to the author, the substances that have been called "hypochlorin" and chlorophyllan are mixtures of this kind.

Leaves of lucerne (*Medicago sativa*) were collected shortly before inflorescence, dried in the dark, and extracted with carbon bisulphide. The residue was treated with alcohol of 85°, which dissolves extractive matters, glucoses, &c., yielding a solution with a very intense

green colour. After distilling off the alcohol, the residue is completely soluble in carbon bisulphide.

The yield is about 20 kilos of colouring matter per hectare of lucerne, and hence 2 grams of active matter per square metre at a height of 0·3 metre is sufficient to ensure the growth of the plant.

From the carbon bisulphide and alcoholic extracts, the author has separated four distinct and definite chlorophylls, which have been analysed, and will be described subsequently.

One of these has the composition $C_{28}H_{45}NO_4$, and cryometric determinations give for its molecular weight 425 (Cal. 459). The author distinguishes it by the name *α-medicagophyll*. In order to isolate it, the solid extract is macerated with cold alcohol, and the residue from the alcoholic solution thus obtained is treated with ether. The latter is distilled off and the residue treated with pentane, which at first, owing to the presence of traces of ether, dissolves all the chlorophyll, but on the addition of more pentane, a portion of the colouring matter is precipitated and remains permanently insoluble in this solvent. The product is soft and amorphous, with bluish reflection, and great tinctorial power. It is soluble in carbon bisulphide but insoluble in water, and is free from extractive matters, gum, tannin, glucoses, and vegetable acids, and only leaves 0·88 per cent. of ash. Its solution in glacial acetic acid has an intense green colour with red dichroism. α-Medicagophyll is heavier than water. It is insoluble in concentrated potassium hydroxide solution, but dissolves in very dilute solutions of alkalis, from which it is precipitated by acids and even by sodium chloride. When dissolved in dilute potassium hydroxide solution, and heated with ammoniacal silver nitrate, it yields a silver mirror, a reaction which is shared by all the chlorophylls examined by the author. C. H. B.

Carminic acid. By E. Schunck and L. Marchlewski (*Ber.*, 1894, **27**, 2979—2985; compare v. Miller and Rohde, Abstr., 1894, i, 94).—Pure carminic acid is prepared by treating cochineal extract with lead acetate, decomposing the lead salt with sulphuric acid in presence of alcohol, and evaporating to dryness at the lowest possible temperature; the residue agrees in properties with the "carminic acid" described by others, and is further purified by dissolving it in cold absolute alcohol and precipitating with ether, benzene, or chloroform. It then crystallises from alcohol, at the ordinary temperature, in small, red prisms. Aqueous solutions of carminic acid, when evaporated, give an amorphous substance, but no crystals. Crystallised carminic acid, $C_{11}H_{12}O_6$ or $C_{11}H_8O_4 + 2H_2O$, differs little in properties from the amorphous preparations, it darkens at 130°, and blackens without melting at 205°. In alcoholic solution, it shows three ill-defined absorption bands, one in the green and two in the blue; in alkaline solution, they appear in the yellow and green. The *barium* and *calcium salts* are brown, changing to violet with excess of base; the *lead* and *aluminium salts* are also violet, and the *stannous salt* scarlet. Aqueous carminic acid solutions are immediately decolorised by animal charcoal, the latter increasing greatly in volume and becoming gelatinous; this peculiar compound is not

changed by alcohol, but is decomposed into its constituents by alkalis. The *anilide*, $C_{17}H_{13}O_3N + 3H_2O$, is deposited in ruby crystals, darkens at 130°, melts and decomposes at 189—190°, and is hydrolysed by alkalis. It is impossible, at present, to decide in what manner the water is combined in the molecule. J. B. T.

Filicic Acid. By G. Daccomo (*Gazzetta*, 1894, **24**, i, 511—523; compare Schiff, Abstr., 1890, 162).—Copper filicate is obtained as a green, crystalline powder; it has the composition $C_{28}H_{30}O_{10}Cu$, and not that attributed to it by Grabowski (*Annalen*, **143**, 279). The *ammonium* salt, $C_{14}H_{15}O_5{\cdot}NH_4$, is a white, amorphous powder having no definite melting point.

On oxidation with hydrogen peroxide, filicic acid yields an *acid*, $C_{14}H_{16}O_6$; it is a red, amorphous powder, and does not reduce ammoniacal silver nitrate solution. The *potassium* salt, $C_{14}H_{15}O_6K$, is a reddish, crystalline powder, and is very soluble in water or alcohol. On oxidising filicic acid with potassium permanganate, nitric acid, bromine, or iodine, butyric acid is obtained together with a bibasic acid, $C_5H_8O_4$, which is probably dimethylmalonic acid. W. J. P.

Action of Nascent Bromine on Pyrroline, Pyridine, and Pyrazole. By W. Vaubel (*J. pr. Chem.*, 1894, [2], **50**, 367—369).—Pyrroline reacts with rather more than 3 atoms of nascent bromine, the action of the latter being greatly hindered by the polymerisation of the pyrroline. Pyridine and its derivatives, including piperidine, are scarcely attacked, whilst pyrazole, according to the researches of Buchner (Abstr., 1893, i, 432), reacts with 1 atom of bromine. These results are all in accordance with the author's theory of the configuration of the benzene molecule. Phenylpyrazole, on the other hand, according to Balbiano (Abstr., 1893, i, 672), takes up 3 atoms of bromine. A. H.

Synthesis of Pyrroline Compounds from Nitrosoketones. By C. U. Zanetti and E. Levi (*Gazzetta*, 1894, **24**, i, 546—554).—*Ethylic* 2 : 4-*dimethyl*-3-*acetylpyrroline*-5-*carboxylate*, $C_9H_{14}EtO_3N$, is prepared by treating ethylic acetoacetate dissolved in acetic acid with half the quantity of potassium nitrite necessary to convert it into the nitroso-derivative, adding acetylacetone, and then reducing the product with zinc-dust. It crystallises in lustrous white needles, melts at 143°, and gives a red coloration with dilute mineral acids; the corresponding *acid*, which is obtained on hydrolysis with potash, crystallises in acicular tufts melting at 208—210° with evolution of gas. The solution of the ammonium salt gives precipitates with lead, copper, ferric, mercuric, and barium salts.

2 : 4-*Dimethyl*-3-*acetylpyrroline*, $NH<\begin{matrix}CMe\cdot CAc\\ CH-CMe\end{matrix}$, is obtained by distilling the above carboxylic acid; it crystallises in white lustrous needles, melts at 139—140°, and is very soluble in alcohol, ether, ethylic acetate, less so in boiling water, and insoluble in solutions of alkali carbonates. It acts as a feeble base, dissolving in concentrated hydrochloric acid, but separating again on dilution.

On heating the carboxylic acid with acetic anhydride, a *tetramethyl-*

diacetylpyrocolline, $C_4Me_2Ac\langle^{CO\cdot N}_{N\cdot CO}\rangle C_4Me_2Ac$, is formed; it crystallises in long, yellowish needles melting at 206—208°, with slight decomposition, and very sparingly soluble. It has the normal molecular weight in freezing acetophenone. It is hydrolysed by boiling alkalis with re-formation of the acid.

On treating acetylacetone in acetic acid solution with sodium nitrite, adding ethylic acetoacetate and reducing the product with zinc-dust, ethylic 2 : 4-dimethyl-5-acetylpyrroline-3-carboxylate is obtained isomeric with the ethylic salt first described; the corresponding acid melts at 252—254°, the lower temperature given by Magnanini being due to a printer's error. W. J. P.

Königs and Lellmann's Hydroquinoline. By V. Vincenzi (*Gazzetta*, 1894, **24**, ii, 97—100).—Königs dihydroquinoline, $(C_9NH_9)_2$, prepared by reducing quinoline with zinc-dust and ammonia, seems to be a mixture of two isomerides. By extracting the product with alcohol, two yellow amorphous dihydroquinolines can be obtained melting at 172—174° and 184—187° respectively; it is not yet clear whether these substances are identical or isomeric. They both have the normal molecular weight in freezing benzene or acetic acid.

On treatment with nitrous acid, the dihydroquinoline yields a *nitrosamine* which gives Liebermann's reaction. On brominating, the substance melting at 184—187°, an *additive* product, C_9NH_9Br(?), is obtained. W. J. P.

Dihydroquinolines. By A. Ferratini (*Gazzetta*, 1894, **24**, ii, 190—196; compare Abstr., 1893, i, 602).—The properties of the dihydroquinolines, as would be expected, resemble those of the indoles rather than those of the quinolines. It was therefore to be supposed that the trimethyldihydroquinoline prepared by the author (Abstr., 1893, i, 227) would behave like the methylindoles; this was found to be the case, as the hydrogenated quinoline gives the reactions which E. Fischer and P. Wagner (Abstr., 1888, 283) discovered to hold for methylketoles.

Acetyltrimethyldihydroquinoline, $C_9NH_5Me_3Ac$, is obtained on boiling trimethyldihydroquinoline with sodium acetate and acetic anhydride; it crystallises from light petroleum in long, colourless, prismatic needles melting at 100·5—101·5° and is readily soluble in dilute acids. It yields an unstable *aurochloride* and a stable *platinochloride*, $(C_{14}H_{17}NO)_2,H_2PtCl_6$, which crystallises in yellow needles melting and decomposing at 203—204°. The acetyl-derivative is hydrolysed by hot concentrated acids but not by boiling potash.

Benzilidenetrimethyldihydroquinoline, $CHPh(C_9NH_5Me_3)_2$, is prepared by warming the quinoline with benzaldehyde; it is a white crystalline substance melting at 142—144°.

Trimethyldihydroquinolineazobenzene, $C_9NH_5Me_3\cdot N_2Ph$, may be prepared by treating trimethyldihydroquinoline with diazobenzene chloride at 0°. It decomposes on exposure to the air, and yields a *picrate*, $C_{24}H_{22}N_6O_7$, which crystallises in red needles melting and decomposing at 208—209°. W. J. P.

Synthesis of Kynurine. By F. Wenzel (*Monatsh.*, 1894, **15**, 453—468).—The investigations of Kretschky (Abstr., 1881, 827; 1883, 674) have shown that kynurine is a hydroxyquinoline, the hydroxyl group of which is contained in the pyridine ring, and its presence in the oxidation products of cinchonic acid (Abstr., 1887, 164; *Monatsh.*, 1887, **8**, 801, 818) renders it probable that it is a 4′-derivative. In order to obtain a satisfactory proof of its constitution, the author has endeavoured to prepare kynurine synthetically from cinchonic acid, and has succeeded in doing so by a series of reactions, each of which proceeds almost quantitatively.

The starting point for the preparation of kynurine is ethylic cinchonate, which may be prepared by heating potassium cinchonate with potassium ethylic sulphate at 170—180°, but is best obtained by saturating the alcoholic solution of cinchonic acid with hydrogen chloride, the yield being almost quantitative if the excess of alcohol and hydrogen chloride are evaporated off in a vacuum. Ethylic cinchonate, contrary to the statement of van der Kolf and van Leent (Abstr., 1889, 1017), distils without decomposition under 15 mm. pressure at 173°, and then forms a colourless, dispersive liquid which becomes pink after a time. It is best converted into cinchonamide by heating with alcoholic ammonia at 140—150°, the amide being thus obtained in lustrous, colourless needles melting at 178°.

When cinchonamide is treated with bromine and caustic potash, according to Hoogewerff and van Dorp's method, it is converted into 4′-amidoquinoline, a small quantity of *bromo-4′-amidoquinoline* being simultaneously formed. The latter crystallises in colourless, slender needles, sublimes at 105°, and melts, when quickly heated, at 199°. The properties of 4′-amidoquinoline observed by the author agree with those given by Hoogewerff and van Dorp. When treated with nitrous acid it does not yield a diazo-derivative, but is at once converted into 4′-chloroquinoline (compare Marckwald, Abstr., 1894, i, 381), which melts at 29—30° (uncorr.) and boils at 260—261° (corr.) under 744 mm. pressure. It is identical with the chloroquinoline obtained by Skraup by the action of phosphorus pentachloride on kynurine, thus proving that the hydroxyl-group in the latter occupies the 4′-position. To further confirm this, the chloro derivative was converted into the ethyl derivative by heating it with alcoholic sodium ethoxide at 120°, and the ethyl derivative then heated with hydrochloric acid at 190°. The substance thus obtained was proved to be identical with kynurine both by its melting point and crystallographic form.

The *ethylkynurine*, prepared in the above manner, is a colourless oil, which boils at 186·5° under 30 mm. pressure, and possesses basic properties; its *platinochloride*, C_9NH_6OEt,H_2PtCl_6, crystallises with $2H_2O$ in small, prismatic crystals, and melts, after drying, at 213°, and the *aurochloride*, $C_9NH_6OEt,HAuCl_4$, with $1H_2O$ in small lustrous needles melting at 169°. On treatment with hydriodic acid, according to Zeisel's method, it yields no ethylic iodide, and, therefore, contains no ethoxy-group; hence it must be the *pseudo-ethylic* derivative $C_6H_4<\begin{matrix}CO\cdot CH\\ \|\\ NEt\cdot CH\end{matrix}$. An attempt to obtain the ethoxy-derivative by the action of ethylic iodide on the silver compound of kynurine only

resulted in the formation of the pseudo-derivative, and it is therefore probable that kynurine in alkylation always reacts in the tautomeric form, $C_6H_4<\begin{matrix}CO\cdot CH\\ \|\\ NH\cdot CH\end{matrix}$. It appears not improbable that the ketodihydroquinoline, described by Reissert (Abstr., 1888, 276, 694), is identical with kynurine. H. G. C.

Action of Formaldehyde on Quinaldine. By T. METHNER (*Ber.*, 1894, **27**, 2689—2693).—When quinaldine is heated at 100° in a sealed tube with an aqueous solution of formaldehyde, *quinaldinealkine*, $C_9NH_6\cdot CH_2\cdot CH_2\cdot OH$, is formed. The free base melts at 94—95°; the yellow *aurochloride* at 134—135°, turning red; the orange *platinochloride* at 208—209°, turning brown at 200°; and the *mercurichloride*, $C_{11}H_{11}NO,HCl + 3HgCl_2$, at 135—136°. If the alkine is heated with strong sulphuric acid and acetic acid at 150—160°, it yields *vinylquinoline*, $C_9NH_6\cdot CH{:}CH_2$, which was only obtained as an impure oil; the yellow *aurochloride* sinters to a green mass at 113—114°, and melts and decomposes at 152—153°; the orange *platinochloride* turns black at 182°; the *mercurichloride*, $C_{11}H_9N,HHgCl_3$, melts at 151—152°, turning red. When the alkine is reduced with tin and hydrochloric acid, tetrahydroquinaldine is formed.

C. F. B.

α-Alkylcinchonic acids and α-Alkylquinolines: Carboxy- and Hydroxy-derivatives of α-Phenylcinchonic acid. By O. DOEBNER and H. FETTBACK (*Annalen*, 1894, **281**, 1—15; compare Abstr., 1888, 299; 1889, 410).—α-Alkylcinchonic acids are formed when a mixture of an aldehyde and pyruvic acid is heated with an aromatic amine; compounds have been obtained in this way from orthamidobenzoic acid and ortho- and par-amidophenols.

2′-Phenylquinoline-1 : 4′-dicarboxylic acid, $C_9NH_4Ph(COOH)_2$, is prepared by heating a mixture of benzaldehyde, pyruvic acid, and orthamidobenzoic acid in alcoholic solution for six hours; it forms minute, colourless needles which melt and decompose above 300°. The *silver* salt is anhydrous, and the *magnesium* salt crystallises with $1H_2O$. Carbonic anhydride is eliminated when the acid is heated with soda-lime, with formation of α-phenylquinoline.

No quinoline derivative can be obtained in this way from paramidobenzoic acid, the *compound* formed having the constitution $COOH\cdot C_6H_4\cdot NH\cdot CO\cdot C(CH{:}CHPh){:}N\cdot C_6H_4\cdot COOH$. It is almost insoluble in alcohol, but may be recrystallised from glacial acetic acid, separating from it in minute needles which melt and decompose above 300°. The analogous *meta*-derivative closely resembles it in properties.

1-Hydroxy-2′-phenylquinoline-4′-carboxylic acid, $OH\cdot C_9NH_4Ph\cdot COOH$, is formed from orthamidophenol in the manner already indicated. It is deposited from glacial acetic acid in lustrous yellow needles which melt at 247°; the *silver*, *copper*, and *calcium* salts are well defined substances.

1-Hydroxy-2′-phenylquinoline is formed when carbonic anhydride is eliminated from the foregoing acid by distillation; it crystallises from

methylic alcohol in quadratic plates and melts at 59°. The *platinochloride* crystallises in dark yellow needles, and the *picrate* separates from alcohol in yellow needles which melt at 152°.

3-Hydroxy-2′-phenylquinoline-4′-carboxylic acid is obtained from paramidophenol. Recrystallised from dilute hydrochloric acid, it contains 1 mol. H_2O; fusion does not occur below 320°. The *silver* salt is unstable, and the *calcium*, *lead*, and *copper* salts are well defined. When distilled, the acid yields *3-hydroxy-2′-phenylquinoline*, which crystallises from water in slender, white needles melting at 218°. The *picrate* melts at 201°. M. O. F.

α-Alkylcinchonic acids and α-Alkylquinolines: Amido-derivatives of α-Phenylcinchonic acid. By O. Doebner and E. Ferber (*Annalen*, 1894, **281**, 15—24).—*αα′-Diphenylphenanthroline-γγ′-dicarboxylic acid*, $CH<\begin{matrix}CPh=\!=N\\ C(COOH)\end{matrix}>C_6H_2<\begin{matrix}N=\!=CPh\\ C(COOH)\end{matrix}>CH$, is obtained by heating a mixture of benzaldehyde and pyruvic acid with metaphenylenediamine hydrochloride in alcoholic solution for three hours. It separates from hot alcohol in minute, reddish-brown needles which melt at 235°. The *silver* salt decomposes at 100°. The *zinc* salt contains $1H_2O$, and the *magnesium* salt is a reddish-yellow powder of the composition $C_{26}H_{14}N_2O_4Mg + MgO$.

αα′-Diphenylphenanthroline, $\begin{matrix}CPh:N\\ |\\ CH:CH\end{matrix}>C_6H_2<\begin{matrix}N=CPh\\ |\\ CH:CH\end{matrix}$, is formed when the foregoing acid is distilled with soda-lime. The *platinochloride* decomposes at 100°.

2-Dimethylamido-2′-phenylquinoline-4-carboxylic acid,

$$NMe_2\cdot C_9NH_4Ph\cdot COOH,$$

is prepared by heating the mixed alcoholic solutions of benzaldehyde, pyruvic acid, and metamidodimethylaniline for two hours. It is deposited from alcohol in minute, reddish-yellow needles melting at 275°. The *silver* salt is anhydrous, the *lead* and *copper* salts each contain 1 mol. H_2O, and the *zinc* salt $2\frac{1}{2}$ mols. H_2O. On distillation, the acid yields *2-dimethylamido-2′-phenylquinoline*, $NMe_2\cdot C_9NH_5Ph$, the *platinochloride*, *dichromate*, and *picrate* of which have been analysed; the last named melts at 180°. M. O. F.

Synthesis of Isoquinoline. By C. Goldschmidt (*Ber.*, 1894, **27**, 2795).—The preparation of isoquinoline from cinnamaldoxime has been recently described (Abstr., 1894, i, 552), the yield being 2 per cent.; if the aldoxime is heated on the water bath with phosphoric anhydride and dry infusorial earth (3 parts), the yield is increased to 10 per cent. J. B. T.

A Platinic Compound of Glyoxaline. By L. Balbiano (*Gazzetta*, 1894, **24**, ii, 101—104; compare Abstr., 1893, i, 674).—A double *compound*, $(C_3H_4N_2)_2PtCl_4$, of platinic chloride and glyoxaline is obtained on boiling glyoxaline with sodium platinochloride solution; it forms a microcrystalline, yellow powder, insoluble in nitro-hydro-

chloric acid and most other solvents. The same substance is obtained on heating glyoxaline platinochloride at 180—205°, but cannot be prepared by boiling an aqueous solution of the platinochloride; in the latter case a mixture of platinum with platinous chloride is deposited. W. J. P.

Methylglyoxalidine or Lysidine. By A. Ladenburg (*Ber.*, 1894, **27**, 2952—2957).—Methylglyoxalidine was first prepared by A. W. Hofmann; an increased yield of purer substance is obtained by distilling ethylenediamine hydrochloride (1 mol.) with sodium acetate (2 mols.); it boils at 195—198°, and melts at 105°, not at 221—224° and 85° respectively, as Hofmann states. The *urate* crystallises in triclinic prisms; $a : b : c = 0{\cdot}48736 : 1 : 0{\cdot}51207$; it is soluble in about 6 parts of water at 18°; lysidine itself is a specific for both chronic and acute gout. The *hydrogen tartrate*, $C_4H_8N_2,C_4H_6O_6$, crystallises in monoclinic prisms; $a : b : c = 0{\cdot}4588 : 1 : 0{\cdot}2931$, $\beta = 63° 5'$; a full crystallographic description of both salts is given. The hydrochloride is crystalline and hygroscopic. The *mercurichloride*,

$$C_4H_8N_2,HCl,3HgCl_2,$$

crystallises in colourless prisms. The *methyl-derivative*, $C_5H_{10}N_2$, is colourless and crystalline, and melts at 90°. The *hydrochloride* and *platinochloride* have also been prepared; the former is crystalline. J. B. T.

Preparation of Thiouvinuric acid (Amidothiazolecarboxylic acid). By C. Boettinger (*Arch. Pharm.*, 1894, **232**, 349—351).—Amidothiazolecarboxylic acid hydrobromide is prepared by intimately mixing tribromopyruvic acid (3 parts) with thiocarbamide (2 parts) at ordinary temperatures, the violence of the action being moderated by the addition of a little absolute alcohol. The product is dissolved in alcohol, evaporated to dryness, the residue treated successively with carbon bisulphide and cold water, and the acid purified by recrystallisation from hot water. J. B. T.

Urazoles and Triazoles. By G. Pellizzari and G. Cuneo (*Gazzetta*, 1894, **24**, i, 499—511).—Hydrazodicarbonamide may be prepared by heating a mixture of carbamide and a salt of hydrazine (compare Curtius and Heidenreich, Abstr., 1894, i, 166). On heating the carbonamide at 180—250°, it evolves ammonia and yields *urazole*, $\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}\!\!>\!NH$ or $\begin{matrix}C(OH){:}N\\ |\\ N{:}C(OH)\end{matrix}\!\!>\!NH$; it forms colourless crystals, melting and decomposing at 244°. It is soluble in water or alcohol, and crystallises unaltered from hydrochloric acid. It gives a red coloration with ferric chloride or sulphuric acid containing a little nitric acid, and reduces ammoniacal silver nitrate in the cold. Urazole decomposes carbonates and reddens litmus. The *ammonio*-derivative, $C_2O_2N_3H_2{\cdot}NH_4$, is obtained in colourless crystals, and gives off ammonia at 100°. The *argento*-compound is an amorphous, white powder, whilst the *barium*-derivative forms colourless, transparent crystals containing $3H_2O$. The *triplumbic*-derivative, $C_2O_2N_3Pb_3$, is obtained

as a white precipitate, and most of the compounds with the other heavy metals are insoluble in water.

On heating an anhydrous mixture of biuret with a hydrazine salt at 150—160°, ammonia is evolved and urazole is formed together with a little hydrazodicarbonamide; a 97 per cent. yield of the latter substance is obtained if carbamide is used in place of biuret.

Triazole (compare Blodin, Abstr., 1892, 735) may be prepared by heating urazole with phosphorous pentasulphide at 180—200°.

$$\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}\!\!>\!NH - O_2 = \begin{matrix}\dot{C}H{:}N\\ |\\ N{:}CH\end{matrix}\!\!>\!NH.$$

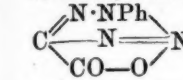
W. J. P.

Oxidation of Formazyl Compounds. By H. v. Pechmann and P. Runge (*Ber.*, 1894, **27**, 2920—2930; compare Abstr., 1894, i, 240).—When ethylic formazylformate is oxidised by means of amylic nitrite and hydrochloric acid in alcoholic solution, it is converted into *ethylic diphenyltetrazoliumcarboxylate chloride*, $COOEt\cdot C\begin{matrix}N\cdot NPh\\ |\\ N{:}NPhCl\end{matrix}>$, which crystallises with 1 mol. alcohol in colourless prisms, effloresces in the air, and melts and decomposes at 195—198°.

This reaction is characteristic of all the formazyl compounds. The free base corresponding with the chloride cannot be isolated pure, but probably has the formula $COOEt\cdot C\begin{matrix}N\cdot NPh\\ |\\ N{:}NPh\cdot OH\end{matrix}>$, being formed from the direct product of oxidation by intramolecular change, the hydroxyl group passing from one nitrogen atom to the other. The formula ascribed to these compounds is confirmed by the fact that when the chloride just described is submitted to dry distillation it yields nearly one-third of its weight of azobenzene. The oxidation products are all remarkably stable towards acids, but are easily reduced by alkaline reducing agents to the original formazyl compounds. The aqueous solutions of the free bases have an alkaline reaction and absorb carbonic anhydride from the air, but only yield red resinous substances on evaporation. The salts, on the other hand, crystallise well, and form neutral solutions in water.

Ethylic diphenyltetrazoliumcarboxylate chloride is very readily soluble in water and gives crystalline precipitates of the *bromide*, *nitrate*, *nitrite*, *iodide*, *chromate*, and *phosphate*, when the corresponding sodium or potassium salts are added to its solution. Zinc-dust reduces it to ethylic formazylformate, whilst alkaline reducing agents form a salt of the free acid. Subcutaneous injections of the chloride produce sickness and affect the circulation, death being finally brought about from paralysis of the heart.

Diphenyltetrazoliumcarboxylic acid chloride, $COOH\cdot C\begin{matrix}N\cdot NPh\\ |\\ N{:}NPhCl\end{matrix}>$, may be obtained by the hydrolysis of the ethylic salt just described, or by the oxidation of formazylformic acid. It forms long, colourless needles, melts and decomposes at 256—257°, and is only sparingly soluble in water. The *nitrate* crystallises in lustrous tablets and melts at 207°.

When the free acid is boiled with water or with sodium carbonate solution, a lactone-like compound, which is the corresponding *betaïne*,  , is formed. It separates from water in lustrous, twinned crystals, and melts at 161°. Dilute acids dissolve it with formation of the corresponding salts of diphenyltetrazoliumcarboxylic acid hydroxide. When it is heated, azobenzene is produced. This formation of an anhydro-compound is an additional confirmation of the formula ascribed to this series of compounds.

Diphenyltetrazolium chloride, $HC\begin{matrix}<\\ \end{matrix}\begin{matrix}N\cdot NPh\\ |\\ N{:}NPhCl\end{matrix}$, may be obtained by the oxidation of formazylhydride or by boiling the chloride of the carboxylic acid just described with alcohol, or heating it or its ethylic salt with hydrochloric acid at 160—180°. It crystallises in stellate groups of lustrous needles, and melts and decomposes at 268°. The *platinochloride* forms orange-yellow prisms, the *aurochloride* melts at 209°, and the *iodide* at 237°.

Triphenyltetrazolium chloride, $PhC\begin{matrix}<\\ \end{matrix}\begin{matrix}N\cdot NPh\\ |\\ N{:}NPhCl\end{matrix}$, is prepared from formazylbenzene, and crystallises in lustrous needles which melt and decompose at 243°. The *platinochloride* melts at 237°, the *bromide* at 255°.

Diphenylparatolyltetrazolium chloride, $PhC\begin{matrix}<\\ \end{matrix}\begin{matrix}N\cdot NPh\\ |\\ N{:}NCl\cdot C_7H_7\end{matrix}$, is obtained from *h*-phenyl-*α*-paratolylformazylbenzene, and melts at 229°.

Benzeneazodiphenyltetrazolium chloride, $PhN{:}N\cdot C\begin{matrix}<\\ \end{matrix}\begin{matrix}N\cdot NPh\\ |\\ N{:}NPhCl\end{matrix}$, from benzeneazoformazylbenzene, crystallises in brownish-yellow prisms with a violet iridescence, and melts and decomposes at 249°. The solution of the base is yellowish-brown. A. H.

Constitution of the Additive Compounds of the Cinchona Alkaloïds with Ethylic Iodide. By Z. H. Skraup (*Monatsh.*, 1894, **15**, 433—436).—The author has examined the action of oxidising agents on the additive compounds of ethylic iodide with the cinchona alkaloïds in the expectation that the pyridine ring of the so-called "first half" would be opened. The results obtained in the case of cinchonine ethiodide have not confirmed this supposition, but are of interest, inasmuch as they confirm the author's previous supposition that the ethyl group combines with the nitrogen atom of the quinoline ring of the "second half" of the molecule.

The hydriodide of cinchonine ethiodide was treated with the requisite quantity of silver nitrate to remove the hydrogen iodide, potassium permanganate gradually added to the resulting aqueous solution in the cold, and the product, after filtering from manganese dioxide, was precipitated successively with lead acetate, mercuric chloride, and cadmium chloride. From the first two precipitates, no crystalline products could be obtained, but from the last a substance was separated, crystallising from water in pointed prisms of the colour of

chromium trioxide. It melts and decomposes at about 200°, and has the composition $C_{12}H_{12}NO_2I + H_2O$, the water of crystallisation being readily given off. From its composition and properties, it appears probable that it is an additive compound of cinchonic acid and ethylic iodide, and this has been confirmed by its direct formation from these two substances. It follows, therefore, that in the original cinchonine ethiodide the ethyl group is in combination with the nitrogen atom of the quinoline group of the second half of the alkaloïd molecule.

When cinchonic acid ethiodide is treated with silver chloride, it is converted into the corresponding *ethochloride*, which crystallises in colourless prisms and melts at 229°. H. G. C.

Action of Water on Trihydriodocinchonine. By G. Pum (*Monatsh.*, 1894, **15**, 446—452).—The author has previously shown (Abstr., 1893, i, 180) that trihydriodocinchonine is converted by alcoholic potash into cinchonine and isocinchonine, and by silver nitrate into β-cinchonine and isocinchonine, whilst Lippmann and Fleissner (Abstr., 1893, i, 736), by heating the same compound with water at 150—160° in a sealed tube, obtained cinchonine, isocinchonine, and a new base, allocinchonine. The author has therefore examined the action of water at the ordinary pressure on trihydriodocinchonine, and finds that it is slowly but completely decomposed with formation of cinchonine and isocinchonine as the sole products. He has also repeated the experiments of Lippmann and Fleissner, but, in this case also, was unable to obtain any allocinchonine. This difference in the results may possibly be due to the presence of the allocinchonine as an impurity in the original cinchonine employed by Lippmann and Fleissner, or to some slight variation in the conditions under which the reaction was carried out. H. G. C.

Technical Preparation of Cocaïne from its Associated Alkaloïds. By A. Einhorn (*Ber.*, 1894, **27**, 2960).—A polemical reply to Liebermann (compare Abstr., 1894, i, 557). A patent has been granted for the author's method of synthesising cocaïne, and the process is employed technically. J. B. T.

Carnic acid. By M. Siegfried (*Ber.*, 1894, **27**, 2762—2763).—Carnic acid ("Fleischsäure"), $C_{10}H_{15}N_3O_5$, is contained in muscle as a compound of phosphoric acid, phosphorcarnic acid, and forms readily soluble salts of calcium and barium, which decompose when their solutions are boiled, the corresponding phosphate being deposited. It forms a ferric compound, *carniferrin*, which is soluble in alkalis, and only gives the reactions for iron after being in contact with the reagents for some time. Carnic acid is monobasic, and yields crystalline salts of *zinc*, *copper*, and *barium*. The *silver* salt, $C_{10}H_{13}N_3O_5Ag_2 + 2H_2O$, is sparingly soluble; the second atom of silver probably replaces the hydrogen atom of an imido-group. Carnic acid also unites with 1 mol. of hydrogen chloride; the substance formed reacts with silver nitrate only on heating.

From its properties, carnic acid appears to be identical with antipeptone, and has been observed among the products of tryptic digestion. A. H.

Organic Chemistry.

Liquid Ethane and Propane. By A. Hainlen (*Annalen*, 1894, **282**, 229—245).—A detailed account of the experiments of which the results have already been published by L. Meyer (this vol., i, 1). A. H.

Preparation of the Paraffins. By F. Kluge (*Annalen*, 1894, **282**, 214—228).—A detailed account of the experiments of which the results have already been published by L. Meyer (this vol., i, 2). A. H.

Formation of Dicarbon Compounds from Carbon Bisulphide at Low Temperatures. By V. Meyer (*Ber.*, 1894, **27**, 3160—3161).—When carbon bisulphide is chlorinated at 20—40°, the carbon tetrachloride formed is found to contain perchlorethylene and perchlorethane. M. O. F.

New Class of Compounds of the Inactive Hydrocarbons. By J. A. Wanklyn and W. J. Cooper (*Chem. News*, 1894, **70**, 211—212).—The authors find that hydrocarbons from Russian kerosene produce a reduction in temperature when mixed with acetic acid, and regard it as indicating combination, and, moreover, the products begin to distil at a lower temperature than would be the case if they were only mixtures of their components. D. A. L.

Ferric Thiocyanate. By L. Andrews (*Chem. News*, 1894, **70**, 165—166).—Spectroscopic examination of solutions of ferric thiocyanate in amylic alcohol distilled from phosphoric acid, and in absolute ethylic alcohol, show that the absorbent power of such solutions diminishes more rapidly than the concentration; and inasmuch as the molecular conductivity of such solutions is found to diminish, with increasing dilution, in about the same ratio as the reciprocal of the absorption coefficient, the falling off of the colour cannot be due to electrolytic dissociation; and, as hydrolysis is out of the question in the present case, neither Magnanini's nor Ostwald's theory seems capable of fully explaining the behaviour of ferric thiocyanate in solution. Compared with aqueous solutions, a solution containing 0·0625 milligram of ferric thiocyanate per c.c. of amylic alcohol transmitted 42 per cent. of light of wave-length 587, about the same amount as an aqueous solution containing 0·247 milligram per c.c. D. A. L.

Linalol and Licareol. By P. Barbier (*Bull. Soc. Chim.*, 1894, [3], **11**, 261).—Referring to Bouchardat's paper (Abstr., 1893, i, 544), the author claims priority of discovery (Abstr., 1892, 1236) of the tendency of acetic anhydride to cause the conversion of the alcohol-

of this class into isomerides. He also denies the identity of linalol and licareol. L. T. T.

Constitution of Rhodinol from Oil of Pelargonium. By P. Barbier and L. Bouveault (*Compt. rend.*, 1894, **119**, 334—337).—The principal constituent of oil of pelargonium is a somewhat oily liquid with a strong odour of roses; it boils at 115—116° under a pressure of 10 mm.; sp. gr. at 0° = 0·8866; rotatory power of a column 20 cm. long −12° 28′. When heated at 150—160° with a large excess of acetic anhydride, it yields (together with a small quantity of a hydrocarbon which boils at 60—80° under a pressure of 10 mm.) an acetate which boils at 120° under a pressure of 10 mm., and has a somewhat agreeable odour; sp. gr. at 0° = 0·9158. This acetate combines with one molecular proportion of bromine. When hydrolysed, the liberated alcohol has its original boiling point, but its odour has become weaker, the sp. gr. has fallen to 0·8825, and the rotatory power of a column 200 mm. long has fallen to −7° 12′. Phenylic isocyanate acts on the alcohol as a dehydrating agent, and yields only diphenylcarbamide.

This rhodinol from pelargonium is a primary alcohol, and when carefully oxidised yields an aldehyde containing the same number of carbon atoms. The yield is, however, somewhat small, a large quantity of condensation products of high boiling point being formed at the same time. The aldehyde has a mixed odour of peppermint and lemon, and boils at 105—108°, but cannot be separated from the excess of alcohol that always accompanies it. It yields a liquid oxime boiling at 140—150°, and this is converted by acetic anhydride into a nitrile, $C_{10}H_{15}N$, which boils at 112—113° under a pressure of 11 mm., and combines with one molecular proportion of bromine. The aldehyde has the composition $C_{10}H_{16}O$.

The products of the oxidation of rhodinol contain an acid, $C_{10}H_{18}O_2$, which boils at 149—150° under a pressure of 10 mm., and combines with one molecular proportion of bromine. More energetic oxidation yields acetone and an acid, $C_7H_{12}O_4$, which boils without decomposing above 300° under the ordinary pressure and at 250° under a pressure of 10 mm. It is a bibasic acid, and does not combine with bromine; when boiled with aniline, it yields an anilide which crystallises in slender, colourless needles melting at 206—207°, somewhat soluble in alcohol, especially on heating, but only slightly soluble in ether. When boiled with acetic anhydride, the acid yields a very viscous anhydride, $C_7H_{10}O_3$, which boils at 180° in a vacuum. This new bibasic acid is *α-methyladipic acid*; attempts to prepare it synthetically were unsuccessful.

The rhodinol of oil of pelargonium differs from its isomerides, lemonol (geraniol) and licarhodol, with which it has hitherto been confounded, in that it does not readily lose water with formation of a terpene, and is not attacked by hydrochloric acid in the cold. Moreover, the hydrochloride, when heated with potassium acetate, yields rhodinol acetate, whereas the hydrochlorides of its isomerides yield a terpene. It is a primary alcohol with a ring-constitution, but with only one ethylenic function. C. H. B.

Syntheses in the Sugar Group. By E. FISCHER (*Ber.*, 1894, **27**, 3189—3232).—This paper is a compilation of the work accomplished by the author and his collaborators, together with the more important researches of other chemists in the same domain since the year 1891. It thus forms a continuation of the paper on the same theme (Abstr., 1890, 1223) which the author delivered as a lecture before the German Chemical Society. The first section deals with experimental methods, and in the next section the present aspect of the sugar group is discussed, the known aldoses and ketoses being tabulated together with the mono- and di-basic acids and polyhydric alcohols derived from them. The author then deals with the stereochemistry of the sugar group, and from this leads up to the configuration of the sugars and allied compounds. He then describes a nomenclature which expresses the configuration of these compounds in a more concise manner, thus glucose is denoted "*hexose* + − + +" or "*hexapentolal* + − + +." These formulæ do not, however, represent, as did those of van't Hoff, the influence of a single asymmetrical carbon atom on the optical properties of the molecule, but only the position of one substituent to the right or left side of the configuration formulæ (compare Abstr., 1891, 1173 and 1444). The last two sections are under the following headings: "Influence of Configuration on Chemical and Physical Properties" and "Importance of Stereochemical Results in regard to Physiology." The papers quoted have all appeared in this Journal, principally as abstracts; their collation has, however, enabled the author to draw some most important and suggestive deductions. A. R. L.

Amount of Magnesia and Lime in Sugar Juice. By J. WEISSBERG (*Bied. Centr.*, 1894, **23**, 715; from *Oester.-Ungar. Zeits. Zuckerind. u. Landw.*, **22**, 153—155).—Ignited magnesia is about 300 times less soluble in 10 per cent. sugar solution than lime, and is less soluble in boiling sugar solutions than in cold solutions. Inasmuch as magnesia is so sparingly soluble in pure sugar solutions, and much more soluble in sugar-lime solutions, it was thought possible to prepare a magnesia sucrate, or, at least, a lime-magnesia sucrate; neither compound could, however, be obtained. Beetroot juice (100 c.c.) was treated with milk of lime in the usual manner with addition of ignited magnesia (1 gram). After the first saturation, a few c.c. of milk of lime and some milk of magnesia were added to the juice, which was then saturated a second time. The filtered solution yielded an ash containing CaO, 0·351 gram; MgO, 0·021 gram; or about 17 times as much lime as magnesia.

Limestone containing 2 or 3 per cent. of magnesium carbonate would, therefore, have no appreciably injurious effect on the composition of the products, since magnesia is so slightly soluble in sugar juice. N. H. J. M.

Iodide of Starch Reaction. By C. MEINEKE (*Chem. Zeit.*, 1894, **18**, 157—160).—An aqueous solution of iodine may be added to a solution of starch until the liquid is decidedly yellowish, without developing any blue colour. The smallest amount of potassium iodide,

however, is sufficient to give the reaction. This seems at first a confirmation of Mylius's statement, that iodide of starch contains potassium or hydrogen iodide as an essential constituent; but the author's investigation proves that the presence of a soluble iodide is not at all necessary for obtaining the blue compound. The author has tabulated the results of a large number of experiments, showing that the compound is also formed, more or less completely, in the presence of other salts such as potassium, sodium, ammonium, calcium, and barium chloride; potassium, sodium, ammonium, and magnesium sulphate; potassium alum; potassium and sodium biborate. L. DE K.

Maltol. By H. KILIANI and M. BAZLEN (*Ber.*, 1894, **27**, 3115—3120; compare J. Brand, Abstr., 1894, i, 270).—Maltol forms characteristic metallic salts. The *zinc* salt separates in colourless needles which retain water; the *copper* salt is anhydrous. The *calcium* salt crystallises in silky needles containing $5H_2O$; it becomes yellow in contact with air or in a vacuum, owing to loss of water. The *lead*, *barium*, *cadmium*, *potassium*, and *ammonium* salts are also crystalline. *Benzoylmaltol*, $C_6H_5O_2{\cdot}OBz$, is colourless and neutral; it melts at 115—116°.

Oxidation of maltol with potassium permanganate gives rise solely to acetic acid and carbonic anhydride, the same products being formed on treating the aqueous solution with silver oxide. Maltol is not acted on by hydriodic or sulphuric acids, and no change occurs when the solution in alcohol or acetic acid is saturated with hydrogen chloride. Bromine has no action on maltol dissolved in chloroform, but the aqueous solution yields a syrupy acid which loses bromine very readily.

It is clear from these observations that the constitutional formula suggested for maltol (*loc. cit.*) must be considerably modified, and the authors prefer to regard it as a methylpyromeconic acid.

M. O. F.

Nitrogenous Compound prepared from "Fungus-cellulose." By E. WINTERSTEIN (*Ber.*, 1894, **27**, 3113—3115; compare Abstr., 1894, ii, 425).—The author has already shown that the cellulose obtained from various fungi contains a considerable quantity of nitrogenous constituents which are not of a proteïd nature. Further investigation has shown that when the fungus-cellulose is heated with hydrochloric acid, it yields glucosamine hydrochloride, identical with the product obtained in a similar manner from chitine (Abstr., 1885, 53; 1886, 329). Whether the constituent which gives rise to the formation of glucosamine is identical with chitine has not yet been ascertained. H. G. C.

Action of Halogen Hydracids on Formaldehyde in presence of Alcohols. By L. HENRY (*Compt. rend.*, 1894, **119**, 425—426).—The reaction recently described by Favre (this vol., i, 14) was previously observed by the author (*Bull. Acad. Sci. Belge*, [3], **25**, 439), and also by P. Henry (Abstr., 1892, 27); the former investigated the action of hydrobromic and hydriodic acids as well as that of hydrochloric acid. C. H. B.

Chloro-formoxime. By R. Scholl (*Ber.*, 1894, **27**, 2816—2822).—This substance, which has recently been described by Nef (this vol., i, 10), was obtained by the author in 1892, having been regarded as the dihydrochloride of fulminic acid. The observations of Nef are fully confirmed. M. O. F.

Cause of the Transformation of Ethylic α-Bromacetoacetate into Ethylic γ-Bromacetoacetate. By A. Hantzsch (*Ber.*, 1894, **27**, 3168—3169; compare Abstr., 1894, i, 227).—This remarkable intra-molecular change is due to the agency of traces of hydrogen bromide, and is checked by the presence of moisture. M. O. F.

Free Acids from Beeswax. By T. Marie (*Compt. rend.*, 1894, **119**, 428—431).—The free acid present in beeswax was regarded by Brodie as a single substance; but Schalfesew and Nafzger have shown that it is a mixture. The author finds that the separation of the acids cannot readily be effected by Heintz's method of fractional precipitation with metallic acetates, but is easily attained by means of fractional crystallisation from methylic alcohol, provided all organic substances except the acids are first removed.

The wax is extracted with boiling methylic alcohol, and, after the greater part of the solvent has been distilled off, the cooled and crystallised residue is pressed in order to remove the oleïc compounds and the colouring matters. The cake is melted, washed several times with boiling water, decolorised with charcoal, and filtered through paper; it is then heated with lime and potash-lime until evolution of hydrogen ceases, in order to destroy myricin. The powdered mass is next suspended in water, heated to boiling, and saturated with dilute hydrochloric acid, the calcium salts which precipitate being collected, washed, dried, and treated with boiling alcohol and benzene to remove neutral substances. The acids are then liberated, and, after crystallisation from methylic alcohol, melt at 79—80°.

The mixture of acids is well triturated with 30 times its weight of methylic alcohol, heated carefully to boiling, and filtered at 60°. The filtrate contains chiefly cerotic acid, which crystallises on cooling. This treatment is repeated with successively diminishing volumes of alcohol until the residue melts at 78°. The dissolved product will then melt at 76°. A single crystallisation from ethylic alcohol raises this melting point to 77·5°.

Crude cerotic acid has been described as a single substance, but in reality it contains from 30 to 40 per cent. of analogous acids. The author is investigating the properties of the pure acids and its salts. C. H. B.

Constitution of Ricinoleic and Ricinostearolic acids. By A. G. Goldsobel (*Ber.*, 1894, **27**, 3121—3129; compare J. Baruch, Abstr., 1894, i, 170).—Ricinostearolic acid,

$$C_6H_{13}\cdot CH(OH)\cdot CH_2\cdot C{:}C[CH_2]_7\cdot COOH,$$

when treated with concentrated sulphuric acid, yields ketohydroxystearic acid, $C_6H_{13}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot COOH$. The latter gives with hydroxylamine, ketoximehydroxystearic acid,

$$C_6H_{13}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot C(NOH)\cdot[CH_2]_7\cdot COOH,$$

and this acid is converted by phosphorus pentachloride into an oil, which, when heated with fuming hydrochloric acid at 180—200°, yields γ-decalactone, $\begin{matrix}CH_2\cdot CH(C_6H_{13})\\ |\\ CH_2 \text{———} CO\end{matrix}>O$, amidocaprylic acid, α-hexyltrimethylenimine, $C_6H_{13}\cdot CH<\begin{matrix}CH_2\\ NH\end{matrix}>CH_2$, and azelaïc acid.

Ketohydroxystearic acid forms silky crystals, and melts at 84—85°. The *barium* and *silver* salts are colourless, and the *ethylic* salt melts at 54·5°; the *acetyl* derivative is a yellow oil. The *phenylhydrazide* is formed when the acid is heated with phenylhydrazine at 150°.

Ketoximehydroxystearic acid is an oil which is decomposed into hydroxylamine and ketoxystearic acid by dilute mineral acids. On heating it with alcoholic ammonia and adding hydrochloric acid, the product exhibits the characteristic reaction of pyrroline derivatives.

The *hydrochloride* of α-hexyltrimethylenimine is hygroscopic, and yields the yellow *platinochloride*. *Amidocaprylic acid*,

$$NH_2\cdot[CH_2]_7\cdot COOH,$$

melts at 172°, and its *hydrochloride* at 147°. M. O. F.

Turkey-red Oil. By P. Juillard (*Bull. Soc. Chim.*, 1894, [3], **11**, 280—286).—This is a continuation of the author's previous work (Abstr., 1892, 819, and 1893, i, 455) on the action of sulphuric acid on castor-oil and on ricinoleic acid. Diricinic acid, $O(C_{17}H_{32}\cdot COOH)_2$, is a bibasic acid. It is a thick, oily liquid, soluble in alcohol in all proportions, whilst its ethylic and methylic salts are but sparingly soluble in alcohol. Ricinoricinic acid, $OH\cdot C_{17}H_{32}\cdot CO\cdot O\cdot C_{17}H_{32}\cdot COOH$, best prepared by heating ricinoleic acid at 170—180°, is the first member of the series of polymerides of ricinoleic acid, and is a monobasic acid. *Dihydroxystearosulphuric acid*, $SO_4H\cdot C_{17}H_{33}(OH)\cdot COOH$, closely resembles ricinosulphuric acid in properties. *Dihydroxystearic acid*, $C_{18}H_{36}O_4$, is very soluble in alcohol and ether, sparingly in light petroleum, and melts at 66—68°. A solid acid, $C_{36}H_{70}O_7$, was obtained, melting at 70—73°, which appears to be a molecular compound of dihydroxystearic acid with ricinoleic acid. *Isoricinoleic acid*, $C_{18}H_{34}O_3$, is an oily liquid, soluble in alcohol and in light petroleum, and appears to be a ketonic acid. L. T. T.

Action of Thionyl Chloride on Organic Acids and Aldoximes. By C. Moureu (*Compt. rend.*, 1894, **119**, 337—340).—See this vol., ii, 43.

Preparation of Thiodiglycollic acid. By J. M. Lovén (*Ber.*, 1894, **27**, 3059—3060).—An improved method of preparation. 95 grams of crystallised chloracetic acid is placed in a large beaker, and a solution, heated to 35°, of 145 grams of crystallised sodium carbonate in 50 c.c. of water is added. 45 grams of sodium hydroxide is dissolved in water, so that the solution has a volume of 100 c.c., one half is saturated with hydrogen sulphide, and then the two halves are added simultaneously to the solution in the beaker, which is meanwhile shaken or stirred. The pasty mass is allowed to stand

for three hours; 110 grams of strong sulphuric acid is then added, carefully, but without cooling, and the hot solution is filtered, and allowed to cool. After six hours, the crystals of crude thiodiglycollic acid are collected and dried; they weigh about 70 grams, and contain 10—15 per cent. of sodium hydrogen sulphate. The crude crystals are dissolved in hot water (50 c.c. for every 70 grams), and the solution is filtered; on cooling, 53 grams of very pure thiodiglycollic acid is deposited.

The mother liquor from the crude crystals, evaporated until it weighs 270 grams, is cooled to 40°, and then filtered. The filtrate, on further cooling, yields crystals of thiodiglycollic acid; these are purified by recrystallisation from the mother liquor of the first crop of pure crystals, and then weigh 10 grams. 63 grams of the pure acid are thus obtained from 95 grams of chloracetic acid, a yield which is 84 per cent. of the theoretical. C. F. B.

Hydrolysis of Ethylic Dicarboxyglutaconate. By H. W. Bolam (*Ber.*, 1894, **27**, 3061—3062).—When ethylic dicarboxyglutaconate (1 mol.) is boiled with 10 per cent. aqueous barium hydroxide (4 mols.), it is partly hydrolysed, malonic and another acid,

$$OH{\cdot}CH{:}C(COOH)_2\ (?),$$

being formed. The barium salt of the latter acid resembles that prepared by Ruhemann and Morell (Trans., 1891, 749) from ethylic amidoethylenedicarboxylate. C. F. B.

Leucine from Pancreatic Digestion. By R. Cohn (*Zeit. physiol. Chem.*, 1894, **20**, 203—209).—The present research brings forward evidence to show that the leucine obtained in a pancreatic digestion of proteïd matter is not a single substance, but a mixture of several isomeric substances. W. D. H.

Derivatives of Dimethylalloxan. By W. Techow (*Ber.*, 1894, **27**, 3082—3089).—*Dimethyldialuric acid*, $CO<\begin{matrix}NMe{\cdot}CO\\NMe{\cdot}CO\end{matrix}>CH{\cdot}OH$, is best obtained by the action of sodium amalgam on a thick magma of amalic acid (tetramethylalloxantin) and water, the whole being well shaken and cooled. The product is poured into hot dilute hydrochloric acid, and filtered, the whole series of reactions being carried out quickly, as the acid is very soon reddened by the air, especially when moist. The acid forms compact prisms, reddens at 100°, melts and decomposes at 170°, and reduces silver and copper solutions in the cold. The *potassium* salt, $C_6H_7N_2O_4K$, forms voluminous flakes, which soon assume a deep blue colour in the air, and the *barium* salt, $C_{12}H_{14}N_4O_8Ba + 2H_2O$, forms microscopic crystals.

Dichlorodimethylbarbituric acid, $CO{:}(NMe{\cdot}CO)_2{:}CCl_2$, is readily obtained by the action of phosphorus pentachloride on amalic acid at 180°; it crystallises from alcohol in delicate, white needles or well-developed prisms, melts at 157° (uncorr.), and on long continued boiling with water loses hydrogen chloride, with formation of dimethylalloxan. When treated with sodium amalgam, it is con-

verted into the dimethylbarbituric acid, already described by Mulder (Abstr., 1879, 618). *Dimethylvioluric acid*, $CO:(NMe\cdot CO)_2:C:N\cdot OH$, is prepared by the action of hydroxylamine hydrochloride on dimethylalloxan, and forms hard, well-developed crystals melting at 124°. It is strongly acid, liberating carbonic anhydride from carbonates. The *potassium* salt, $C_6H_6N_3O_4K$, forms a deep bluish-violet, flocculent, crystalline mass, the *ammonium salt*, $C_6H_6N_3O_4NH_4 + H_2O$, deep red crystals, which change to pale red on heating, and the *barium* salt, $C_{12}H_{12}N_6O_8Ba + H_2O$, a heavy, red precipitate. When added in small quantities to hot concentrated nitric acid, it is converted into *dimethylnitrobarbituric acid*, $CO:(NMe\cdot CO)_2:CH\cdot NO_2$, which separates from acetone as a white, microcrystalline mass, melting at 148°; the *sodium* salt, $C_6H_6N_3O_5Na + 4H_2O$, crystallises in slender, yellow prisms.

The *ammonium salt of dimethylthionuric acid*,

$$CO:(NMe\cdot CO)_2:CH\cdot NH\cdot SO_3NH_4 + 2H_2O,$$

is obtained by saturating a concentrated solution of ammonia with sulphurous anhydride and warming with solid ammonium carbonate and dimethylalloxan, and separates, on cooling, in fascicular aggregates of slender, lustrous needles; the water of crystallisation is evolved at 105°, the salt simultaneously assuming a red colour, and, on further heating, it decomposes completely at 180°. On adding barium chloride to its solution, the *barium salt*, $C_6H_7N_3O_6SBa$, separates in silky crystals. The free acid is an amorphous mass, which is readily soluble in water, has strongly acid properties, and, on boiling in aqueous solution, is converted into sulphuric acid and *dimethyluramil*, $CO:(NMe\cdot CO)_2:CH\cdot NH_2$. The latter compound is also obtained by the reduction of dimethylvioluric acid or of dimethylnitrobarbituric acid, but is best prepared by boiling ammonium dimethylthionurate with fuming hydrochloric acid, diluting with water, and neutralising with ammonium carbonate. Dimethyluramil then separates in snow-white, silky flakes, which melt and decompose at about 200°, and, on exposure to the air in the moist condition, quickly become dark red. It reduces silver and copper solutions, is decomposed by alkalis, even by ammonium carbonate, but unites with acids to form unstable salts; the *hydrochloride* forms small, hard crystals, which lose hydrogen chloride in a vacuum, and the *platinochloride*, $(C_6H_9N_3O_3)_2,H_2PtCl_6$, crystallises in yellow prisms.

Dimethylpseudouric acid, $CO:(NMe\cdot CO)_2:CH\cdot NH\cdot CO\cdot NH_2$, is prepared by the action of a concentrated solution of potassium cyanate on dimethyluramil. It forms small, white crystals, reddens at 100°, melts and completely decomposes at 210°, and reduces silver solutions. The *potassium* salt, $C_7H_9N_4O_4K + H_2O$, is crystalline, and the *copper* salt, $(C_7H_9N_4O_4)_2Cu + 2H_2O$, is a pale green precipitate, which loses its water of crystallisation at 105°, the colour changing simultaneously to yellowish-brown. H. G. C.

Action of Iodine and Potassium Hydroxide on Uric Acid. By E. Bryk (*Monatsh.*, 1894, **15**, 519—529).—Kreidl has described a method for the estimation of uric acid by treating it with potassium

hydroxide and iodine, and subsequently titrating with thiosulphate (Abstr., 1893, ii, 558). The author finds that the action of iodine on a solution of uric acid, to which potassium hydroxide has been previously added, depends on the proportion in which the substances are present and also on the temperature. If only a small excess of potassium hydroxide is employed, say in the proportion of 2·25 mols. to 1·3 atoms of iodine and 1 mol. of uric acid, and the mixture is kept cool, a yellow insoluble substance separates. This on analysis gave the numbers C = 28·37—26·86, H = 4·39—3·71, N = 28·53—29·19, and on solution in potash or sulphuric acid and subsequent reprecipitation with water gave uric acid. When a similar mixture is warmed, potassium urate, carbonic anhydride, and ammonia are formed. The employment of a larger proportion of potassium hydroxide, say 4 mols. to 2 atoms of iodine and 1 mol. of uric acid, gives rise to allantoïn and carbonic anhydride; the yield of the former is good (40—50 per cent.). G. T. M.

Polymeric Ethoxysulphonethylenesulphinic Lactone. By G. Walter (*Ber.*, 1894, **27**, 3043—3045).—When an aqueous solution of free ethoxysulphonethylenesulphinic acid is evaporated to dryness, there is formed, in addition to the lactone soluble in water, already described (Abstr., 1893, i, 459), an insoluble polymeric modification, which has, however, the same melting point and chemical properties as the soluble variety. It can be converted into the latter by hydrolysing it with baryta water, liberating the free acid from the barium salt so obtained, and evaporating the solution of this acid. C. F. B.

Some Derivatives of Ethoxymethylsulphone. By G. Walter (*Ber.*, 1894, **27**, 3045—3049; compare Abstr., 1893, i, 459).—Ethoxymethylsulphone, $OH\cdot C_2H_4\cdot SO_2\cdot CH_3$, on treatment with phosphorus pentachloride, yields *chlorethylmethylsulphone*,

$$Cl\cdot C_2H_4\cdot SO_2\cdot CH_3,$$

which melts at 8·5—9°. When this is treated with ammonia, there are formed, besides ammonium chloride, the hydrochlorides of *primary* and *secondary methylsulphonethylamine*, $NH_2\cdot C_2H_4\cdot SO_2\cdot CH_3$ and $NH(C_2H_4\cdot SO_2\cdot CH_3)_2$. The first *hydrochloride* forms deliquescent prisms, and the corresponding orange *platinochloride* melts and decomposes at 220—221°. The second *hydrochloride* melts at 202—203°, the orange *platinochloride* at 159—160°, and the *benzoyl-derivative* at 131°; the free base forms stable crystals.

If ethoxymethylsulphone is allowed to remain with cold, strong, sulphuric acid, and the mixture then added to a magma of water, ice, and barium carbonate, *barium methylsulphonethylene sulphate*,

$$Ba(SO_4\cdot C_2H_4\cdot SO_2\cdot CH_3)_2 + H_2O,$$

is formed. This is readily hydrolysed, by boiling with water, yielding barium sulphate, sulphuric acid and ethoxymethylsulphone; ammonia converts it into the amines described above. C. F. B.

Action of Sulphuric Acid on Bromothiophen. By A. Töhl and K. Schultz (*Ber.*, 1894, **27**, 2834—2839; compare Abstr., 1894, i, 117 and 276).—In addition to the results already described (*loc. cit.*), it is found that slightly fuming sulphuric acid converts tribromothiophen into tetrabromothiophen, the sulphonic acids of dibromo- and tribromothiophen being also formed in small quantities. If fuming acid is employed, perbromodithienyl and tetrabromothiophen are formed. M. O. F.

Synthesis of Metachlorotoluene and of Symmetrical Chloroxylene from Ethylic Acetoacetate. By A. Klages and E. Knoevenagel (*Ber.*, 1894, **27**, 3019—3025; compare this vol., i, 48).—*Dihydrometachlorotoluene* [Me : H_2 : Cl = 1 : 2 : 3 : 5] is prepared by the action of phosphoric chloride on 3-methyl-Δ_2-keto-tetrahydrobenzene; the intermediate methyltrihydrodichlorobenzene could not be isolated, it is a highly refractive liquid with an aromatic odour, boils at 78—80° (25 mm.), at 160—170° under atmospheric pressure, and is volatile with steam, some of the compound being decomposed. The yield is 60 per cent. of the ketone employed. The ketone is regenerated by the action of sulphuric acid (95 per cent.), a tertiary alcohol being first formed which is either identical with the ketone or is converted into it by intramolecular rearrangement. The *dibromide* is unstable and could not be purified; on warming alone or with quinoline, hydrogen bromide is eliminated and metachlorotoluene is formed.

2:3:5-*Dihydrochloro-xylene* [Me:Me = 1 : 3] is prepared in a similar manner to the toluene derivative from 3 : 5-dimethyl-Δ_2-keto-tetrahydrobenzene, which it closely resembles; it boils at 78—80° (15 mm.), and at 176—178° under ordinary pressures with little decomposition, darkens on exposure to air, and regenerates the ketone on treatment with sulphuric acid. The yield is 70 per cent. of the ketone employed.

The *dibromide* is unstable and is readily converted into *symmetrical chloro-xylene*, a highly refractive mobile liquid boiling at 190—191°; its vapour rapidly attacks the skin. The *sulphonic acid* crystallises in lustrous plates, is readily soluble in water, and melts at 65—68°. The *sodium* and *barium salts* crystallise in plates. The *sulphonic chloride* and the *sulphonamide* crystallise in colourless needles melting at 48—49° and 189—190° respectively. The position of the sulphonic group has not been determined. J. B. T.

Mercuric Phenoxides and Naphthoxides. By E. Desesquelle (*Bull. Soc. Chim.*, 1894, [3], **11**, 263—269).—*Mercuric β-naphthoxide chloride*, $ClHg{\cdot}O{\cdot}C_{10}H_7$, obtained by shaking together aqueous solutions of mercuric chloride and potassium β-naphthoxide, crystallises in colourless prisms soluble in alcohol, insoluble in water. For medical purposes, the author proposes for this substance the name *β-sublimonaphthol*. *Mercuric β-naphthoxide*, $Hg(O{\cdot}C_{10}H_7)_2$, forms microscopic crystals, almost insoluble in the usual solvents but slightly soluble in boiling phenol. Acetic acid acts on it with development of heat, yielding *mercuric β-naphthoxide acetate* as a white, crystalline substance, soluble in alcohol, almost insoluble in water.

Mercuric phenoxide chloride forms colourless crystals melting about 210°, soluble in phenol or in a boiling alcoholic or aqueous solution of phenol. *Mercuric phenoxide hydroxide*, OH·Hg·OPh, is formed when a large excess of potassium phenoxide is employed, and crystallises in stellar groups of prisms. With acetic acid, this compound yields *mercuric phenoxide acetate*, crystallising in colourless prisms. The author has not been able to obtain the derivative $Hg(OPh)_2$.

L. T. T.

New Colour Reaction of Iridol. By E. Nickel (*Chem. Zeit.*, 1894, **18**, 531).—When a solution of iridol (Abstr., 1894, i, 48) in aqueous alcohol is warmed with a solution of mercuric chloride (2 parts) and sodium nitrite (1 part) in water (40 parts), a beautiful, violet coloration, having a bluish tinge, is developed. This reaction was previously described by the author as characteristic of vanillin, and, indeed, there is no essential difference between the colorations produced by the two substances. A. R. L.

Thioaniline (m. p. 105°), and a new Isomeride. By K. A. Hofmann (*Ber.*, 1894, **27**, 2807—2816).—The author has shown that Merz and Weith's thioaniline is orthodiamidophenylic sulphide, $S(C_6H_4·NH_2)_2$; orthodiamidophenylic bisulphide is also formed when aniline is heated with sulphur, and may be converted into orthodiamidophenylic sulphide by the addition of lead oxide to its solution in boiling aniline.

Paradiamidophenylic sulphide is prepared by heating a mixture of aniline, aniline hydrochloride, and sulphur for 6—7 hours at 175°; it crystallises from boiling water in colourless, lustrous plates, which melt at 85·5°. The *hydrochloride* yields an emerald-green solution when heated with fuming sulphuric acid for half an hour at 100°. On adding lead peroxide to the solution in alcoholic hydrochloric acid, a green coloration is produced, changing to deep blue. The *benzoyl* derivative melts at 234°, and the *diacetyl* derivative at 185°; the corresponding derivatives from orthodiamidophenylic sulphide melt at 255° and 213—215° respectively.

Paradiamidophenylic bisulphide, $C_{12}H_{12}N_2S_2$, is associated with the foregoing compound. It forms colourless needles, and melts at 80°; the *diacetyl* derivative melts at 205°; it yields paradiamidophenylic sulphide when strongly heated. The solution of the *hydrochloride* in alcohol is coloured deep cherry-red by lead peroxide, and the colourless solution in strong sulphuric acid becomes violet when heated. Sulphur is precipitated when hydrogen sulphide is passed through a solution of the hydrochloride in dilute hydrochloric acid, amidophenyl mercaptan remaining dissolved. When paradiamidophenylic bisulphide is diazotised, decomposed in alcoholic solution with copper powder, and saturated with hydrogen sulphide, thiophenol is produced, and parabromothiophenol is formed on displacing the amido-group with bromine. M. O. F.

Suggested Non-existence of Isopropyleneparamidophenol. By A. Michaelis and K. Luxembourg (*Ber.*, 1894, **27**, 3005—3009).—Haegele's work on this compound has been repeated, and his

results are confirmed as regards its formation from pure acetone; it melts at 172—174°, is slowly hydrolysed by boiling with water, and more readily with dilute acids (compare Hantzsch and Freese, Abstr., 1894, i, 572, and this vol., i, 24). The calcium hypochlorite reaction is a delicate test for paramidophenol; the acetate reacts more readily than the hydrochloride; the dilute hypochlorite solution should be added gradually, as the violet colour is destroyed by excess of it.

J. B. T.

Chlorides of Hydroximic Acids and their Products of Change. By A. Werner (*Ber.*, 1894, **27**, 2846—2850).—*Orthonitrobenzhydroximic chloride*, $NO_2 \cdot C_6H_4 \cdot CCl{:}NOH$, is formed when dry chlorine is passed into a solution of orthonitrobenzaldoxime in chloroform; it melts at 92—94°. The *meta*-derivative melts at 94—95°, and the *para*-compound at 115—117°.

Orthonitrobenzenylamidoxime, $NO_2 \cdot C_6H_4 \cdot C(NH_2){:}NOH$, is obtained by warming the acid chloride with alcoholic ammonia. It forms bright yellow needles, which contain $1H_2O$; the substance loses water at 80°, and melts at 141—142°. The *para*-derivative melts at 165—167°.

Metadinitrobenziledioxime peroxide, $\begin{matrix} O \cdot N{:}C \cdot C_6H_4 \cdot NO_2 \\ | \quad\quad | \\ O \cdot N{:}C \cdot C_6H_4 \cdot NO_2 \end{matrix}$, is produced when metanitrobenzhydroximic chloride is warmed with concentrated aqueous potash. It melts at 183—185°. The *para*-compound melts at 197—198°.

Orthonitrobenzenylpiperidoxime, $NO_2 \cdot C_6H_4 \cdot C(C_5NH_{10}){:}NOH$, is obtained by mixing ethereal solutions of piperidine and orthonitrobenzhydroximic chloride. It melts at 132—133°, and the *meta*-derivative melts at 159—160°. The *para*-compound melts at 166—167°.

M. O. F.

Action of Amidoacetal on Orthonitrobenzoic Chloride and Paranitrobenzoic Chloride. By W. Löb (*Ber.*, 1894, **27**, 3093—3097).—*Orthonitrobenzoylamidoacetal*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2,$$

is obtained in a manner analogous to the benzoyl derivative (Abstr., 1893, i, 300), and crystallises from ether on the addition of light petroleum in stellate groups of colourless needles melting at 70—71°. On treatment with cold fuming hydrochloric acid, it is converted into *orthonitrohippuraldehyde*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CHO$, an amorphous, pale yellow substance, which softens at 90°, decomposes at a higher temperature, and reduces Fehling's solution. It could not be directly converted into the corresponding *orthonitrohippuric acid*, but the latter was obtained by the action of orthonitrobenzoic chloride and alkali on glycocine; it crystallises from hot water in long, narrow plates melting at 188°, and gives crystalline precipitates with silver and lead salts.

Orthamidobenzoylamidoacetal, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, is prepared by the reduction of the nitro-compound with zinc dust and acetic acid in alcoholic solution, and crystallises from light petroleum containing a little ether, in druses of colourless needles, melting at

80—81°. By the action of concentrated hydrochloric acid, not only are both the ethyl groups eliminated, but also the elements of water, with formation of the *anhydride of orthamidohippuraldehyde*, a white, amorphous compound, which decomposes at 300° without previously melting; it has the empirical formula $C_9H_8N_2O$, but is probably a polymeride.

Paranitrobenzoylamidoacetal is prepared in a similar way to, and closely resembles the ortho-derivative; it melts at 82°, and, with hydrochloric acid, yields *paranitrohippuraldehyde*, which forms colourless, amorphous flakes, softens at 100°, and reduces Fehling's solution. Like the ortho-compound, it cannot be converted into the corresponding *acid*, which was prepared from paranitrobenzoic chloride and glycocine, and forms colourless prisms melting at 129°.

When paranitrobenzoylamidoacetal is treated with reducing agents, it does not, like the ortho-derivative, yield the amido-compound, but is converted into the azoxy- or azo-derivative according to the strength of the reducing agent employed. *Parazoxybenzoylamidoacetal*, $ON_2[C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2]_2$, is obtained by the action of zinc dust and acetic acid in the cold, and crystallises in pale red plates melting at 182°.

Parazobenzoylamidoacetal, $N_2\cdot[C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2]_2$, is formed if the solution is boiled with zinc dust and acetic acid; it crystallises in long, narrow, carmine-red plates, melting at 202·5°.

H. G. C.

Derivatives of Amidoaldehyde. By H. Heller (*Ber.*, 1894, **27**, 3097—3102).—E. Fischer has already shown that amidoacetal combines with aldehydes and acid chlorides, and that the products are resolved by the action of hydrochloric acid into the corresponding derivatives of amidoaldehyde. The author, in the present paper, describes a number of these derivatives.

Paramethoxybenzylideneamidoacetal, $OMe\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot CH(OEt)_2$, is obtained by the action of amidoacetal on anisaldehyde, and forms a colourless oil having a bluish fluorescence, and boiling at 190° (corr.) under 12 mm. pressure. It yields salts, of which the *oxalate*, melting at 138°, is the most stable. On reduction with sodium in alcoholic solution, it yields *paramethoxybenzylamidoacetal*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot CH_2\cdot CH(OEt)_2,$$

which is a colourless, slightly fluorescent liquid boiling at 187° (corr.) under 12 mm. pressure; its *oxalate* crystallises in colourless needles melting at 174°.

Paramethoxybenzylamidoaldehyde, $OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot CH\cdot CHO$, is obtained in the form of the *hydrochloride* by the action of hydrochloric acid on the foregoing compound at 50°; it crystallises with $\frac{1}{2}H_2O$, reduces Fehling's solution strongly, and with alkalis yields the free aldehyde, which is amorphous. The *phenylhydrazone hydrochloride* crystallises from alcohol in lustrous, colourless plates which become brown at 150°; it is converted by alkalis into the oily free *phenylhydrazone*.

Anisylamidoacetal, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, is prepared

by the action of anisic chloride on a cooled ethereal solution of amidoacetal, the *hydrochloride* separating out in lustrous, white plates which are converted into the free base by alkalis; the latter forms yellowish, prismatic needles melting at 60—61°. With hydrochloric acid, it yields *paramethoxyhippuraldehyde*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CHO$, the *hydrochloride* of which separates out in colourless cube-shaped crystals melting at 128° with decomposition. The free aldehyde forms amorphous flakes and reduces Fehling's solution strongly. The *phenylhydrazone* crystallises in colourless needles, which soon become reddish, and on heating turn brown and then melt at 126°; the *oxime* crystallises in slender, white needles, and melts and decomposes at 163°. By the action of bromine, the aldehyde is converted into *metabromoparamethoxyhippuric acid*, $C_{10}H_{10}O_4NBr$, which forms slender, white needles and melts at 161—162°; its *silver* salt crystallises from hot water in stellate groups of needles. When strongly heated with concentrated hydrochloric acid, it is converted into metabromanisic acid.

Orthohydroxybenzylideneamidoacetal, $OH\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot CH(OEt)_2$, obtained by the action of salicylaldehyde on amidoacetal, crystallises in yellow tablets melting at 32°, and boils at 188° (corr.) under 15 mm. pressure. *Orthohydroxybenzoylamidoacetal* is prepared by heating methylic salicylate with amidoacetal at 120°, and crystallises from light petroleum in yellowish, rhombic plates melting at 54°. By the action of strong hydrochloric acid, it is converted into the *hydrochloride of orthohydroxyhippuraldehyde*,

$$OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CHO,HCl,$$

which forms white tablets, and melts at 150° with decomposition. The free aldehyde has only been obtained as a syrup with strongly reducing properties; its *phenylhydrazone* crystallises in pale yellow needles, and melts and decomposes at 134°; the *oxime* forms needles melting at 142°. H. G. C.

Phthalyl Compounds of Amidoacetal. By W. Alexander (*Ber.*, 1894, **27**, 3102—3105).—*Phthalyldiamidoacetal*,

$$C_6H_4[CO\cdot NH\cdot CH_2\cdot CH(OEt)_2]_2,$$

is obtained by the action of phthalic chloride on amidoacetal in ethereal solution, and separates, on the addition of light petroleum, in colourless needles melting at 90°, and decomposing rather above 100°. The corresponding *aldehyde* is formed by the action on it of hydrochloric acid, the *hydrochloride* being thus obtained as a syrup which reduces Fehling's solution. By the action of alcoholic potash, phthalyldiamidoacetal is converted into *orthobenzoylamidoacetalcarboxylic acid*, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, which separates on the addition of light petroleum to its ethereal solution in stellate groups of colourless needles containing $1H_2O$; it melts and decomposes at about 100°.

Terephthalyldiamidoacetal is prepared in a manner analogous to the phthalyl-derivative, and crystallises in flat needles or plates melting at 165°. The corresponding *aldehyde*, $C_6H_4(CO\cdot NH\cdot CH_2\cdot CHO)_2$, is a bulky, white powder which only dissolves in concentrated hydro-

chloric acid and alkalis; its *phenylhydrazone* forms yellow flakes. *Terephthalyldiamidoacetic acid*, $C_6H_4(CO\cdot NH\cdot CH_2\cdot COOH)_2$, is obtained by the action of bromine on the aldehyde, and crystallises from hot water in needles which melt at 240° with evolution of gas; the *silver* salt is a curdy precipitate which may be recrystallised from hot water, and the *copper* salt an insoluble, crystalline precipitate, which is blue when moist, but becomes green on drying. The acid may be more conveniently prepared by acting on glycocine with terephthalic chloride according to Baumann's method.

Isophthalyldiamidoacetal, obtained in the same manner as its isomerides, melts at 75°; the corresponding *aldehyde* closely resembles the terephthalyl derivative, but cannot readily be converted into *isophthalyldiamidoacetic acid*, which was therefore obtained from glycocine and isophthalic chloride; it forms colourless cubes, and melts with decomposition at about 210°. H. G. C.

Aromatic Nitro-derivatives. By V. Meyer (*Ber.*, 1894, **27**, 3153—3159).—Trinitrobenzoic chloride [$COCl : (NO_2)_3 = 1:2:4:6$] is produced on heating trinitrobenzoic acid with a mixture of the oxychloride and pentachloride of phosphorus. It displays remarkable stability in presence of water, being only slightly decomposed when boiled with it for an hour (compare Sudborough, Trans., 1894, 1030). The solution of trinitrobenzoic acid in alkali (1 mol.) is colourless, and yields a colourless silver salt with silver nitrate; but if excess of alkali is employed, a deep orange-red liquid is formed. On adding acid to this solution, unchanged trinitrobenzoic acid is thrown down; this behaviour is comparable with the development of a deep red coloration exhibited by trinitrobenzene in presence of alkali.

A small quantity of 1:3:5-dinitrobenzoic acid dissolved in dilute alkali forms a colourless solution, becoming deep violet when excess of strong alkali is added. After a few minutes, the liquid loses colour, and on remaining for two hours a further change occurs, and a stable, magenta coloration is developed.

The author criticises the conclusions drawn by Nef regarding the constitution of salts of the nitro-paraffins (this vol., i, 3).

M. O. F.

Reduction of Paradimethylamidobenzoic acid and Paramidobenzoic acid. By A. Einhorn and A. Meyenberg (*Ber.*, 1894, **27**, 2829—2834; compare Abstr., 1894, i, 591).—*Paradimethylamidohexahydrobenzoic acid*, $C_6H_{10}<\begin{matrix}CO\\NHMe_2\end{matrix}>O$, is obtained, in association with hexahydrobenzoic acid, by the reduction with sodium of paradimethylamidobenzoic acid dissolved in amylic alcohol. The acid liquefies at 99—100°, resolidifies at 130°, and finally melts at 218—220°; it contains $2\frac{1}{2}H_2O$. It is a neutral substance, and forms a bright blue *copper* salt; the *platinochloride* melts at 232°.

Paramidohexahydrobenzoic acid, $C_6H_{10}<\begin{matrix}CO\\NH_2\end{matrix}>O$, is formed on reducing with sodium paramidobenzoic acid dissolved in amylic alcohol, hexahydrobenzoic and valeric acids being formed simulta-

neously. On adding the aqueous solution to absolute alcohol, the acid crystallises in small, white plates which melt at 303—304°.

M. O. F.

Isomeric Paramethylenedihydrobenzoic acids. By A. Einhorn and R. Willstäter (*Ber.*, 1894, **27**, 2823—2829; compare Abstr., 1894, i, 523).—In addition to $\Delta^{2,4}$-paramethylenedihydrobenzoic acid, and the acid obtained by Einhorn and Friedländer on hydrolysing the methiodides of ethylic *r*-ecgonine and *l*-ecgonine, there exists a third acid, $C_8H_8O_2$, which remains liquid at −20°. It is prepared by heating $\Delta^{2,4}$-paramethylenedihydrobenzoic acid with alcoholic potash for 48 hours in a reflux apparatus; it boils at 160° (20 mm.), and the *amide* melts at 90°. The crystalline acid (m. p. 55—56°) described by Einhorn and Friedländer is also formed when $\Delta^{2,4}$-paramethylenedihydrobenzoic acid is boiled with alcoholic potash for 12 hours; the *amide* melts at 101—102°. This acid and paramethylenedihydrobenzoic acid, on reduction, yield the same 1 : 4-ethylcyclopentanecarboxylic acid.

It is not yet clear whether the liquid acid just described is structurally different from the substance obtained by Einhorn and Friedländer, or whether the isomerism is geometrical in character.

M. O. F.

Bismuth Salts. By B. Fischer and B. Grützner (*Arch. Pharm.*, 1894, **232**, 460—466; compare Abstr., 1894, i, 416).—The authors prepared basic bismuth salts by heating freshly precipitated bismuth hydroxide with the respective acids. *Basic bismuth paracresotate*, $C_7H_7O{\cdot}COO{\cdot}BiO$, and the *metacresotate* both form needles similar in all respects to the salicylate. No definite basic salts could be obtained from anisic, benzoic, or cinnamic acids. The *tartrate*, $C_4H_4O_6{,}2Bi(OH)_2$, forms an amorphous, electrical, white powder. Attempts to prepare the basic nitrate by the action of the calculated quantity of a 5 per cent. alcoholic solution of nitric acid on freshly precipitated bismuth hydroxide were sometimes successful and sometimes not. The authors were unable to find out the conditions necessary to ensure a successful result. L. T. T.

Hydroxy-derivatives of Phenylbutyric acid. By F. Kopisch (*Ber.*, 1894, **27**, 3109—3113).—In the course of their synthesis of phenyltetrose, Fischer and Stewart (Abstr., 1892, 1447) obtained several hydroxy-derivatives of phenylbutyric acid; the author has subjected these to a further examination in order, if possible, to separate them into optically active compounds. In this he has been unsuccessful; but a number of interesting derivatives have been obtained which are described in the present paper.

Barium phenyltrihydroxybutyrate, $(C_{10}H_{11}O_5)_2Ba$, is obtained by the action of boiling baryta water on the lactone, and forms slender needles. The *strychnine salt*, $C_{21}H_{22}N_2O_2{,}C_{10}H_{12}O_5 + H_2O$, crystallises in microscopic needles or plates, loses its water of crystallisation at 95°, and becomes yellow at 105°. *Nitrophenyltrihydroxybutyrolactone* is obtained by the action of nitric acid of sp. gr. 1·5 on the lactone of the trihydroxy-acid, and crystallises in slender, colourless needles melting at 185° with slight evolution of gas; on boiling with alkalis

it first dissolves, after which a crystalline, yellow precipitate suddenly separates. *Phenylamidodihydroxybutyric anhydride*, prepared by boiling phenylbromhydroxybutyrolactone with ammonia for a short time, forms well-developed, colourless prisms which have a neutral reaction, become brown at 200°, and melt at 215°. It is not altered by boiling with alkalis or heating with phenylhydrazine, and it is therefore uncertain whether it is a lactone or a lactam. *Phenylbromodihydroxybutyranilide*, OH·CHPh·CHBr·CH(OH)·CO·NHPh, obtained by heating the bromolactone with aniline at 100°, crystallises in slender needles melting at 167—168° (uncorr.), and the *phenylhydrazide*, obtained by the action of phenylhydrazine in the cold, forms microscopic, rhombus-shaped plates melting and decomposing at 168—169°. If the bromolactone is warmed with phenylhydrazine, it is converted into *phenylhydroxybenzylhydroxypyrazolidone*, which has probably the constitution $CO<\begin{matrix}CH(OH)\cdot CH\cdot CHPhOH\\ NH\text{———}NPh\end{matrix}$, and crystallises in spherical aggregates of colourless needles melting at 208°.

When the bromolactone is reduced with sodium amalgam, it yields two products having the composition $C_{10}H_{10}O_3$ and $C_{10}H_{10}O_2$ respectively. The former is probably a *phenylhydroxybutyrolactone*, and may be a stereoisomeride of the compound described under the same name by Biedermann (Abstr., 1892, 471). It crystallises from ether in colourless needles, melts at 124—126°, and gives a white crystalline precipitate with phenylhydrazine in ethereal solution. The second compound, separated by means of its solubility in light petroleum, crystallises in large, colourless needles melting at 87—88°, and behaves towards phenylhydrazine in the same manner as the previous compound. Its constitution is unknown. H. G. C.

The Law of Etherification of Aromatic Acids. By V. Meyer and J. J. Sudborough (*Ber.*, 1894, **27**, 3146—3153; compare Abstr., 1894, i, 463).—The nitrophthalic acids behave similarly to substituted benzoic acids as regards the formation of ethereal salts.

Dinitrophthalic acid [NO_2 : COOH : COOH : NO_2 = 1 : 2 : 3 : 4] gives no ethereal salt, whilst the acid [NO_2 : COOH : COOH : NO_2 = 1 : 3 : 4 : 5] yields monalkylic salts. 1 : 2 : 6-Dinitrobenzoic acid gives no ethereal salt.

Tetrachlorophthalic acid, however, yields small quantities of the normal methylic salt, but as the behaviour of 2 : 4 : 6-trichlorobenzoic acid is normal, the authors conclude that the normal methylic salt is analogous in structure to phthalylic chloride, and cannot, therefore, be regarded as a true ethereal salt. Both 2 : 4 : 5- and 3 : 4 : 5-trichlorobenzoic acids yield an ethylic salt. 2 : 4 : 6-Trichlorobenzoic acid was prepared from trichloraniline instead of tribromaniline. M. O. F.

Introduction of Acid Radicles into Ethylic Benzoylacetate. By A. Bernhard (*Annalen*, 1894, **282**, 153—191).—When ethylic cuprobenzoylacetate is treated with benzoic chloride, three substitution compounds are produced. Ethylic dibenzoylacetate, or ethylic α-benzoyl-β-hydroxycinnamate, OH·CPh:CBz·COOEt, has been pre-

viously described (Trans., 1891, 1000), and is converted by bromine into ethylic bromodibenzoylacetate. The *copper* compound crystallises from alcohol in needles melting at 221°.

Ethylic α-benzoyl-β-benzoxycinnamate, OBz·CPh:CBz·COOEt, constitutes about one-half of the neutral products formed by the above reaction. It crystallises from ether in thick prisms, melts at 98°, and is readily soluble in hot alcohol, &c. It gives no coloration with ferric chloride, and is only slowly decomposed by warming with aqueous soda. When treated with sodium ethoxide, it yields ethylic benzoate, together with ethylic α-benzoyl-β-hydroxycinnamate. A similar change is produced by phenylhydrazine, benzoylhydrazine being formed. Bromine also acts in a somewhat similar manner, benzoic bromide and *ethylic α-bromodibenzoylacetate*, $CBrBz_2$·COOEt, being produced. The latter crystallises in elongated tablets, and melts at 109—110°. The same bromo-compound is formed directly by the action of bromine on ethylic dibenzoylacetate and ethylic α-benzoyl-β-acetoxycinnamate. The remainder of the neutral oil referred to above probably consists of *ethylic β-benzoxyisocinnamate*, OBz·CPh:CH·COOEt, although this has not yet been isolated from it in the pure state.

Benzoic chloride reacts in a precisely similar manner with ethylic sodiobenzoylacetate, the action being in both cases exactly analogous to that of benzoic chloride on ethylic acetoacetate (Nef, Abstr., 1894, i, 628).

When ethylic cuprobenzoylacetate is treated with two-thirds of the calculated amount of acetic chloride, the product consists of ethylic β-acetoxyisocinnamate, and a small amount of ethylic benzoylacetoacetate, together with some regenerated ethylic benzoylacetate. Ethylic benzoylacetoacetate (ethylic α-benzoyl-β-hydroxycrotonate), OH·CMe:CBz·COOEt, has been previously described by Bonné (this Journal, 1887, ii, 437). *Ethylic β-acetoxyisocinnamate*,

OAc·CPh:CH·COOEt,

is a neutral substance, and crystallises in long needles melting at 27—28°. It reacts with sodium ethoxide in alcoholic solution to form ethylic acetate and ethylic sodiobenzoylacetate, and behaves in a similar manner with phenylhydrazine, acetylphenylhydrazine being produced.

Ethylic α-benzoyl-β-acetoxycrotonate, OAc·CMe:CBz·COOEt, is obtained by the action of acetic chloride on the copper compound of ethylic benzoylacetoacetate as a neutral, unstable, brown oil, which is readily decomposed by dilute soda, gives a red coloration with alcoholic ferric chloride when left for a few minutes in contact with it, and reacts with sodium ethoxide to form ethylic acetate and ethylic sodiobenzoylacetoacetate.

Ethylic chloroformate reacts with the sodium and copper compounds of ethylic benzoylacetate to form ethylic benzoylmalonate and ethylic β-carbethoxyisocinnamate, a small amount of ethylic dibenzoylsuccinate (Perkin, jun., Trans., 1883, 263) being also formed in the second case.

Ethylic benzoylmalonate, OH·CPh:C$(COOEt)_2$, is a yellowish oil,

which boils at 192—193° under a pressure of 13 mm. It has strongly acid properties, dissolves in sodium carbonate, and gives a red coloration with alcoholic ferric chloride immediately. When distilled with steam, it decomposes quantitatively into ethylic benzoylacetate, carbonic anhydride, and alcohol. Sodium ethoxide, in alcoholic solution, produces the *sodium derivative*, which is a fine, white powder, and reacts with copper acetate yielding the *copper derivative*, which crystallises in dark green needles melting at 180°.

Ethylic carbethoxyisocinnamate, COOEt·O·CPh:CH·COOEt, is a neutral, viscid, yellow oil, which boils at 200—202° under a pressure of 15 mm. It gives no coloration with ferric chloride until the mixture has stood for a considerable time. With sodium ethoxide, it forms ethylic carbonate and ethylic sodiobenzoylacetate, and reacts with phenylhydrazine in an analogous manner, ethylic benzoylacetate, ethylic carbazinate, and 1 : 3-diphenylpyrazolone (m. p. 135°) having been isolated from the product.

It is noteworthy that almost equal quantities of the neutral and acid products are formed by the action of ethylic chloroformate on ethylic sodiobenzoylacetate, whilst with the corresponding derivative of ethylic acetoacetate, the neutral compound is the chief product.

The action of acid anhydrides on ethylic benzoylacetate proceeds in a manner very similar to that of the acid chlorides, as will be seen from the following summary of the products obtained. (1) Acetic anhydride yields ethylic benzoylacetoacetate (20—30 per cent.), a mixture of ethylic β-acetoxyisocinnamate, and ethylic α-benzoyl-β-acetoxycrotonate (20 per cent.), acetophenone (15 per cent.), acetic acid, ethylic acetate, and ethylic benzoylacetate (18—32 per cent.). (2) Benzoic anhydride yields ethylic dibenzoylacetate (50 per cent.), small amounts of tribenzoylmethane and ethylic dehydrobenzoylacetate, ethylic benzoate, benzoic acid, and possibly ethylic β-benzoxyisocinnamate.

Acetic anhydride also acts on ethylic oxalacetate to form *ethylic β-acetoxyfumarate*, which is a neutral oil, gives no coloration with ferric chloride, and reacts with phenylhydrazine to form acetylphenylhydrazine.

The author is of opinion that the difference in behaviour towards alkalis of the two forms of tribenzoylmethane and dibenzoylacetone may be due to physical causes, and is not necessarily to be ascribed to a difference in chemical constitution (compare Claisen, Abstr., 1894, i, 192).

Two formulæ are possible for the derivatives of the β-ketonic acids which contain two acid radicles such as ethylic dibenzoylacetoacetate, $CAcBz_2$·COOEt and OBz·CMe:CBz·COOEt. Both formulæ equally express the neutral character of the compound; if the former of the two formulæ were correct, the same substance should be obtained by the action of acetic chloride on ethylic dibenzoylacetate, and of benzoic chloride on ethylic benzoylacetoacetate, whereas, according to the second formula, two different compounds should be produced.

Experiment shows that the latter is what actually occurs, ethylic

α-benzoyl-β-acetoxycinnamate and ethylic α-benzoyl-β-benzoxycrotonate respectively being formed. The same view is further confirmed by the fact that sodium ethoxide, phenylhydrazine, and bromine always replace that acid radicle which has been last introduced.

If this formula be accepted, there are still two stereoisomeric configurations possible, but at present it is impossible to decide between them with any approach to certainty. A. H.

Vinyltriphenylsulphone (Triphenylsulphonethane). By R. Otto (*Ber.*, 1894, **27**, 3055—3058).—When monochlorethylene dichloride is warmed with sodium benzenesulphinate in alcoholic solution, it yields, not a trisulphone, but the disulphone, $C_2H_4(SO_2Ph)_2$, sodium sulphate and benzenesulphonate being simultaneously formed. When warmed with sodium phenyl mercaptide, NaSPh, in alcoholic solution, however, it yields *vinyltrithiophenyl* (*trithiophenylethane*), $SPh{\cdot}CH_2{\cdot}CH(SPh)_2$. This is an oil having an odour resembling that of lemons; when oxidised with permanganate, it yields ethylenediphenylsulphone and a benzenesulphonate, but, if care is taken to avoid a rise of temperature, *vinyltriphenylsulphone* (*triphenylsulphonethane*), $SO_2Ph{\cdot}CH_2{\cdot}CH(SO_2Ph)_2$, is formed. This is insoluble in water; it is readily hydrolysed by aqueous soda, apparently with formation of glycollic aldehyde. C. F. B.

Indigo. By C. J. van Lookeren and P. J. van der Veen (*Landw. Versuchs-Stat.*, 1894, **43**, 401—426).—The authors have prepared indican from the leaves of plants belonging to the species *Indigofera*, and their results are identical with those obtained by Schunck in his experiments with *Isatis tinctoria* (woad). The sugar, which the authors obtained as a syrup by hydrolysing their indican, was dextro-rotatory, reduced Fehling's solution, gave a brown coloration with alkalis, and was probably identical with ordinary glucose (dextrose). The so-called indigo-gluten is probably a mixture of nitrogenous decomposition products of indican, with a certain amount of the enzyme (rendered inactive) which determines the hydrolysis of indican. Schunck's oxindicanin gives a red precipitate when warmed with Millon's reagent. Experiments are next described which point to the existence of an enzyme as the hydrolyst of indican, thus the hydrolysis of indican proceeds under conditions which exclude the presence of micro-organisms. The quality of the indigo-blue is affected by continuing the lixiviation process too long, which is done in practice, and the cause of this may be the action of bacteria. If the so-called fermentation is protracted, the indigo-blue contains a larger proportion of calcium salts and more indigo-gluten. According to the authors, the usual practice is to employ water at a temperature of 27·5° for the fermentation; better results are obtained by digesting with water at an initial temperature of 55°, the digestion (fermentation) being continued for about seven hours at a temperature of about 28°. The authors find that in the manufacture of indigo-blue, equivalent quantities of lime, potash, or soda may be used instead of ammonia. A. R. L.

Parahydrazidodiphenyl. By H. Müller (*Ber.*, 1894, **27**, 3105—3108).—*Parahydrazidodiphenyl*, $C_{12}H_9 \cdot NH \cdot NH_2$, is prepared by diazotising paramidodiphenyl and reducing the diazo-compound with tin and hydrochloric acid, the *hydrochloride* thus formed being decomposed by alkali and the free base extracted with ether; after crystallisation from hot alcohol, it forms lustrous, colourless plates, melts at 135—136° (uncorr.), and quickly oxidises in the air, especially when moist. The *hydrochloride*, *sulphate*, and *nitrate* all crystallise in colourless plates, and are sparingly soluble in cold water. The *acetyl* derivative, $C_{12}H_9 \cdot N_2H_2Ac$, crystallises in colourless plates melting at 203°, and the *thiocarbamide*, $C_{12}H_9 \cdot N_2H_2 \cdot CS \cdot NHPh$, in colourless needles melting at 182°; the latter dissolves in concentrated sulphuric acid with a deep blue colour.

Parahydrazidodiphenyl readily combines with aldehydes and ketones, including the sugars, but the compounds obtained from the latter do not crystallise well, and are, therefore, of no use for the recognition or isolation of the sugars. *Acetonehydrazonediphenyl*, $C_{12}H_9 \cdot NH \cdot N{:}CMe_2$, is crystalline, melts at 86—87°, and yields an indole when heated at 180° with zinc chloride. *Acetophenonehydrazonediphenyl*, $C_{12}H_9 \cdot NH \cdot N{:}CMePh$, forms colourless plates melting at 148°, and *benzylidinehydrazidodiphenyl*, $C_{12}H_9 \cdot NH \cdot N{:}CHPh$, crystallises in yellowish needles melting at 153°. *Arabinosehydrazonediphenyl*, $C_{12}H_9 \cdot NH \cdot N{:}C_5H_{10}O_4$, is obtained with difficulty in nodular aggregates of slender crystals, and melts, when quickly heated, at 138—140°, with decomposition. The *xylose* derivative has similar properties. *Glucosehydrazonediphenyl*, $C_{12}H_9 \cdot NH \cdot N{:}C_6H_{12}O_5$, forms very slender crystals, melts at 143—144° with evolution of gas, and, on heating with an excess of the hydrazine, yields the *osazone*. *Galactosehydrazonediphenyl* crystallises in stellate groups of colourless needles melting and decomposing at 157—158°. H. G. C.

Stereoisomeric Paraphenylhexahydrobenzoic acids. By B. Rassow (*Annalen*, 1894, **282**, 139—153).—*Paraphenylhexahydrobenzoic acid*, $C_6H_{10} \cdot Ph \cdot COOH$, may be prepared by reducing paradiphenylcarboxylic acid with sodium and boiling amylic alcohol, or by treating the same acid with sodium amalgam in alkaline solution, whereby it is converted into a mixture of tetrahydro-acids, acting on these with hydrobromic acid, and finally reducing the hydrobromides thus obtained by means of sodium amalgam. The crude hexahydro-acid melts at 190—195°; but on crystallisation yields an acid, which melts at 202°, together with a portion of lower melting point, from which an acid, melting at 113°, may be isolated in small quantity by extracting with boiling water, filtering, and adding potassium permanganate to the solution in sodium carbonate until a permanent coloration is produced.

Paraphenylhexahydrobenzoic acid (m. p. 202°) crystallises from dilute acetic acid or ether in lustrous plates. The *silver* salt is insoluble in water, the *sodium* and *ammonium* salts sparingly soluble, and the *potassium* salt readily soluble. A solution of the ammonium salt gives white, insoluble precipitates with barium chloride, calcium chloride, zinc sulphate, and mercuric chloride, whilst the *magnesium*

salt dissolves in hot water. The *methylic salt*, prepared by treating the chloride with methylic alcohol, forms tabular crystals, and melts at 28—30°. On oxidation with potassium permanganate, the hexahydro-acid is converted into a *hydroxy-acid*, which probably has the formula $OH{\cdot}C_6H_9Ph{\cdot}COOH$. It forms a honey-like mass, with an ill-defined melting point of about 145°. This hydroxy-acid loses a molecule of water when boiled with water, a *tetrahydrophenylbenzoic acid* being formed, which melts at 158°, and, since it is not altered by boiling with aqueous soda, is probably a $\Delta^{1,2}$-acid. It at once decolorises alkaline potassium permanganate, and combines with bromine. The *silver salt* of the hydroxy-acid also loses a molecule of water when boiled with water, yielding the *salt* of the tetrahydro-acid. More thorough oxidation converts the hexahydro-acid into benzoic acid.

Isoparaphenylhexahydrobenzoic acid (m. p. 113°) is best obtained by heating the acid of higher melting point with fuming hydrochloric acid at 170—180°. It forms lustrous needles, and dissolves in about 1000 parts of boiling water. The *silver salt* blackens when heated in contact with the solution from which it has been obtained, and is somewhat soluble in hot water. The *sodium*, *potassium*, and *ammonium* salts are all readily soluble in water, and the *calcium* salt moderately so. When the iso-acid is heated with fuming hydrochloric acid, it is partially reconverted into the acid of higher melting point, the same state of equilibrium being reached from either acid, that of higher melting point constituting about 90 per cent. of the mixture. The iso-acid is also converted into benzoic acid by oxidation.

The paper is prefaced by a note by Baeyer, in which he points out that it has been found impossible to obtain stereoisomeric forms of tetrahydro-α- and β-naphthoic acids, and that this result, although, as it is negative, it cannot be considered decisive, is in favour of the view that the valencies of the 6 hydrogen atoms of the benzene ring are perfectly symmetrically arranged.

The results described in the foregoing paper show that in the closely related hexahydrophenylbenzoic acid the differences between the properties of the two stereoisomerides are quite well marked.

A. H.

Tetramethyldiamidodiphenylmethane. By J. Pinnow (*Ber.*, 1894, **27**, 3161—3167).—The action of nitrous acid on tetramethyldiamidodiphenylmethane converts it into a mononitro-derivative, which melts at 87—88°. The further action of nitrous acid gives rise to a *dinitro*-derivative, which crystallises in slender, red needles, and melts at 123—124°. An *isomeride* is produced when a mixture of nitric and sulphuric acids is added to the solution of tetramethyldiamidodiphenylmethane in concentrated sulphuric acid; it crystallises from glacial acetic acid in red prisms, which melt at 191·5° (uncorr.). This compound yields *tetramethyltetramidodiphenylmethane* when reduced with tin and hydrochloric acid; the base crystallises in colourless needles, which melt at 142° (uncorr.). The action of nitric acid on tetramethyldiamidodiphenylmethane in glacial acetic acid solution leads to the formation of nitrosamines and nitramido-derivatives;

dimethyldinitrosamidodiphenylmethane is produced on adding sodium nitrite to the solution of the base in hydrochloric acid (sp. gr. 1·19). It crystallises in slender, pale yellow needles, which melt at 101·5°. A condensation product of tetramethyldiamidodiphenylmethane with formaldehyde appears to be formed when a mixture of dimethylaniline (10 grams), formaldehyde solution (10 grams), and glacial acetic acid (15 grams) is boiled for eight hours; it has the composition $(C_{18}H_{22}N_2)x$.

With diazobenzenesulphonic acid, tetramethyldiamidodiphenylmethane yields a colouring matter, which, on reduction with tin and hydrochloric acid, is resolved into paramidodimethylaniline and paramidobenzenesulphonic acid. M. O. F.

Constitution of the Alkali Compounds of Phenolphthaleïn. By E. Hjelt (*Chem. Zeit.*, 1894, **18**, 3).—According to Armstrong (Proc., 1893, 52), the coloured salts of the phthaleïns assume a quinonoïd structure; this view presupposes, for example, in the case of phenolphthaleïn, that the phthalide ring (lactone ring) is readily disrupted by alkalis. The author's experiments indicate, however, that the hydrolysis of the phthalide ring, $C_6H_4<\begin{matrix}CR_2\\CO\end{matrix}>O$, proceeds much more slowly in the case of phthalide and of meconine than in the case of the aliphatic lactones (Henry, Abstr., 1892, 1303). According to the formula $Ac = \frac{x}{(A - x)t}$ (t in minutes), the following values were found; for phthalide, $Ac = 0{\cdot}0674$ ($A = 10{\cdot}1$); and for meconine, $Ac = 0{\cdot}0298$ ($A = 11{\cdot}2$). The hydroxy-acid corresponding with phenolphthaleïn is unknown, and is probably incapable of existence. A. R. L.

Synthesis and Constitution of Vulpic acid. By J. Volhard (*Annalen*, 1894, **282**, 1—21).—According to Spiegel (Abstr., 1881, 97, 173, 1036; 1882, 1076), vulpic acid is the monomethylic salt of the bibasic pulvic acid, which is converted by alkalis into dibenzylglycollic acid, $OH{\cdot}C(CH_2Ph)_2{\cdot}COOH$, a diketonic acid, symmetrical diphenylketipic acid, $COOH{\cdot}CHPh{\cdot}CO{\cdot}CO{\cdot}CHPh{\cdot}COOH$, being formed as an intermediate product.

In order to prepare vulpic acid synthetically, the author starts from benzylic cyanide, which is converted by ethylic oxalate and sodium ethoxide in alcoholic solution into the *dinitrile* of *diphenylketipic acid*, $CN{\cdot}CHPh{\cdot}CO{\cdot}CO{\cdot}CHPh{\cdot}CN$. This substance crystallises from amylic alcohol in olive-green, lustrous scales, and melts and decomposes at 270°. When hydrolysed with 60 per cent. sulphuric acid, the nitrile is converted into pulvic acid dilactone (70 per cent.), and pulvic acid (14—18 per cent.), a small amount of other products of unknown nature being also formed. When the dilactone is treated with a solution of potash in methylic alcohol and the solution acidified, vulpic acid is obtained, identical with that prepared from *Evernia vulpina*.

Piperidine vulpate forms long, thin, yellow needles melting at 139—142°.

The pulvic acid prepared from the dilactone is also identical in every respect with that obtained by Spiegel. It crystallises with $1C_2H_6O$ in yellowish-red, rhombic prisms, which have the axial ratio 0·5835 : 1 : 0·4337.

Monobromopulvic acid, $C_{18}H_{11}BrO_5$, crystallises in radial groups of yellow tablets, melts at 208—209°, and forms a crystalline *barium salt*.

Dibenzyloxalylcarboxylic acid lactone, $CHPh{:}C<^{CO\cdot CHPh}_{O---CO}$, is contained among the products of hydrolysis of the dinitrile. It forms small needles, and melts at 231—233°.

It follows from this synthesis that pulvic acid is the anhydride of diphenylketipic acid, but it is at present impossible to decide between the formulæ

$$CPh<^{CO\cdot O}_{C(OH)}>C{:}CPh\cdot COOH \text{ and } O<^{C{:}CPh\cdot COOH}_{C{:}CPh\cdot COOH}.$$

A. H.

Pulvamic acids and Ethereal Salts of Pulvic acid. By R. Schenck (*Annalen*, 1894, **282**, 21—44; compare the foregoing abstract).—Pulvamic acid has previously been described by Spiegel (Abstr., 1881, 1076). The *ammonium salt* melts at 218°, and the *potassium salt* crystallises in slender needles with $5H_2O$, whilst the *zinc* and *silver salts* are insoluble and amorphous. It appears to be impossible to displace a second hydroxyl-group in the molecule by the amido-group.

Pulvomethylamic acid, $C_{19}H_{15}O_4N$, is obtained by the action of methylamine on the dilactone. It crystallises in quadratic plates, and melts at 237°. The *methylamine salt* melts at 214°. The *barium salt* is sparingly soluble in water. *Pulvanilic acid*, $C_{24}H_{17}O_4N$, forms compact crystals, and melts at 187—188°. The *ammonium salt* melts at 153°; the *potassium salt* forms yellow crystals with $2H_2O$. *Pulv-α-naphthylamic acid* crystallises in iridescent, reddish-yellow plates, and melts at 211—212°. The *ammonium salt* melts at 208°, and the *barium salt* crystallises from alcohol in slender needles. *Pulvo-β-naphthylamic acid* forms druses of large, reddish-yellow crystals, and melts at 192°. The *ammonium salt* melts indefinitely at about 182°. The *barium salt* forms a crystalline powder.

Methylaniline and diphenylamine do not yield amic acids. *Pulvdimethylamic acid* crystallises in small prisms, and melts at 211°, its *dimethylamine salt* melting at 210°. The acid is quite analogous to pulvamic and pulvmethylamic acids. *Pulvopiperidinic acid* is very unstable, and melts at from 150° to 160°. Its *piperidine salt* melts at 199—220°. The metallic salts are decomposed by boiling with water, piperidine being formed. *Pulvhydroxamic acid* is obtained by heating the dilactone with hydroxylamine hydrochloride, sodium acetate, and acetic anhydride. It crystallises in quadratic plates, and melts at 194°, with evolution of carbonic anhydride; the acid is bibasic to baryta water. Its *monaniline salt* forms plates melting at 163—164°. *Pulvophenylhydrazinic acid* melts at 201—202°, and forms

a *phenylhydrazine salt*, which is more readily soluble in alcohol, and melts at the same temperature. The *ammonium salt* forms pale yellow, slender needles, and melts at 187—188°.

The mon-ethereal salts of pulvic acid may be obtained by the action of potash and an alcohol on the dilactone, or by that of an alkylic iodide on the hydrogen silver salt. The normal ethereal salts form compounds with 1 mol. water and 1 mol. piperidine.

The following have been prepared.

	M. p.	M. p. of piperidine compound.
Methylic vulpate.....	141°	147—148°
Ethylic vulpate	138—139	152—153
Methylic ethylpulvate....	150—151	151
Propylic vulpate.....	95—96	149
Methylic propylpulvate ..	121—122	126
Propylpulvic acid.....	134	—

Ammonia reacts with the normal ethereal salts to form an amide and phenylacetic acid. The amide, $C_{10}H_8O_2N_2$, crystallises in bronze-coloured plates, and melts at 247·5°. When boiled with dilute hydrochloric acid, it yields cyanophenylpyruvic acid (compare the following abstract). A. H.

Derivatives of Diphenylketipodinitrile. By J. Volhard and F. Henke (*Annalen*, 1894, **282**, 45—84; compare the two preceding abstracts).—The hydrolysis of the dinitrile occurs in several stages. *Diphenylketipamidonitrile*, $CN\cdot CPh{:}C(OH)\cdot C(OH){:}CPh\cdot CO\cdot NH_2$, is obtained by treating the dinitrile in the cold with concentrated sulphuric acid. It forms pale yellow needles containing 1 mol. C_2H_6O, and melts and decomposes at 199—200°; it gives a brownish-red coloration with alcoholic ferric chloride. When boiled with aqueous sodium carbonate, the nitrile is decomposed into benzylic cyanide and hydroxyphenylmaleïnimide, $C_{10}H_7NO_3$, which is described later on.

Diphenylketipamidonitrilesulphonic acid, $C_{18}H_{13}O_3N_2\cdot SO_3H$, is obtained by warming a solution of the dinitrile in sulphuric acid on the water bath. It forms microscopic, flat needles, and does not melt below 300°. The *sodium* and *barium salts* are both crystalline.

No diamido-compound was observed among the products of hydrolysis of the dinitrile, but a small amount of pulvamic acid (compare the preceding abstract) is formed. This substance can also be readily obtained by boiling the amidonitrile with hydrochloric acid. The *methylic salt* forms almost colourless, compact crystals melting at 216—217°. When this salt is hydrolysed, pulvic acid, and not an isomeride of vulpic acid, is formed.

The dinitrile readily dissolves in alcoholic potash, forming a *potassium salt*, $C_{18}H_{12}O_2N_2K_2 + 2C_2H_6O$, which crystallises in colourless plates. The *sodium salt* may be prepared in a similar manner. The dinitrile also appears to form an unstable *compound* with 1 mol. HCl. The *monacetate*, $CN\cdot CPh{:}C(OAc)\cdot C(OH){:}CPh\cdot CN$, is obtained by the action of a mixture of acetic acid and acetic anhydride;

it crystallises in lustrous needles, and melts at 208—209·5°. It is insoluble in water, but dissolves in aqueous alkalis, the *sodium salt* crystallising with $3H_2O$ in scarlet needles. The *methylic salt*, prepared from the amorphous red *silver salt*, crystallises in lustrous, yellow needles, and melts at 229—231°. When heated with aqueous ammonia at 100°, the acetate yields benzylic cyanide and phenylacetamide, together with oxalic and oxamic acids. Acetic and benzoic chlorides act on the sodium and silver salts, but only reproduce the monacetate. The *diacetate* is formed when the dinitrile is treated with pure acetic anhydride, and forms greyish-green needles melting at 177—179°. It is insoluble in water and alkalis, and combines with 1 mol. of alcohol to form a *compound*, which can be recrystallised from toluene, and melts at 191—191·5°. Methylic alcohol forms a similar *compound*, which crystallises in colourless granules, and melts and decomposes at 196°. The *compound* with amylic alcohol crystallises in very slender needles. Acetic chloride reacts with the dinitrile to yield the monacetate together with the *monacetate* of the lactone of the semi-hydrolysed dinitrile,

$$CPh\begin{matrix}C(OAc)\cdot C:CPh\cdot CN\\ CO\text{——}O\end{matrix}.$$

This crystallises in canary-yellow needles, and melts at 141—142°. The corresponding *benzoate* crystallises in slender, yellowish needles, melting at 168—168·5°. The *monobenzoate* of the dinitrile is also formed in dark, orange-red granules, melting at 220—224°, which dissolve in alkalis. Phosphorus oxychloride converts the dinitrile into a *chloro-derivative*, $CPh\begin{matrix}CCl\cdot C:CPh\cdot CN\\ CO\text{–}O\end{matrix}$, corresponding in composition with the lactone compounds described above. It crystallises in long, greyish-green needles, and melts at 161—162°. It is insoluble in water and aqueous alkalis, but dissolves in alcoholic potash, and yields a crystalline *barium salt*. When heated with sodium acetate and alcohol, it loses chlorine, forming a *hydroxy-compound* of the formula $C_{18}H_{11}O_3N$, which crystallises in matted, reddish-yellow needles, and melts at 193—194°. When heated with acetic anhydride, this is converted into the acetate of the semi-lactone already described.

Dilute alcoholic ammonia at 100° converts the dinitrile into an *iso-cyanophenylpyruvamide*, $C(OH)\begin{matrix}C(NH)\cdot NH\\ CPh\text{—}CO\end{matrix}$, which crystallises in red needles, and does not melt below 280°. It dissolves in alkalis, and forms crystalline *sodium* and *barium* salts. Amylic nitrite converts it into a *nitro-derivative*, $C_{10}H_7N_2O_2\cdot NO_2$, which melts and decomposes at 246°. When heated with dilute hydrochloric acid, it is very readily converted into *hydroxyphenylmaleïnimide*,

$$C(OH)\begin{matrix}CO\text{—}NH\\ CPh\cdot CO\end{matrix},$$

which is best prepared by heating the amidonitrile or its sulphonic

acid with aqueous sodium carbonate. It crystallises in lustrous, yellow scales, melts at 216—218°, gives a green coloration with ferric chloride, and forms salts with one equivalent of metal. The *ethylic salt* crystallises in long, lustrous needles, resembling the salts of uranium in appearance, and melting at 128—130°. This substance is isomeric with the ethylic phenylcyanopyruvate described by Erlenmeyer, jun. (*Annalen*, 1892, **271**, 172). The latter compound, on hydrolysis, yields a substance which was described by Erlenmeyer as phenylcyanopyruvic acid, but which is identical with hydroxyphenylmaleïnimide. This substance cannot have the constitution ascribed to it by Erlenmeyer, as, when its silver salt is treated with ethylic iodide, it yields the yellow ethereal salt described above, and not the original colourless ethylic phenylcyanopyruvate, CN·CPh·CO·COOEt, by the hydrolysis of which it was obtained. It is, moreover, converted by ammonia into the phenylamidomaleïnimide described below. Acetic anhydride converts hydroxyphenylmaleïnimide into the *acetate*, $C_{10}H_6N_2O_3Ac$, which crystallises in long, white needles melting at 134—135°. *Ethoxyphenylmaleïn-benzoylimide*, $C_{19}H_{15}O_4N$, prepared by treating the yellow ethylic salt with benzoic chloride, crystallises in yellowish needles with a greenish fluorescence, and melts at 105—106°. The isomeric *benzoyl-derivative* obtained from Erlenmeyer's ethylic phenylcyanopyruvate crystallises in colourless prisms, and melts at 102—103°.

Phenylamidomaleïnimide, $NH_2·C\begin{matrix}CO—NH\\ CPh·CO'\end{matrix}$, is obtained by the action of alcoholic ammonia on ethoxyphenylmaleïnimide, and has also been obtained from the chloro-semilactone described above, and from the neutral ethereal salts of pulvic acid, a proof that it contains no cyanogen group. It crystallises in thin, golden-yellow, lustrous plates, and melts at 248—249°. The corresponding *piperidide*, $C_{15}H_{16}O_2N_2$, is formed when ethoxyphenylmaleïnimide is heated with piperidine, and crystallises in orange-coloured needles melting at 155—156·5°.

Ethoxyphenylmaleïc anhydride, $C(OEt)\begin{matrix}CO—O\\ CPh·CO'\end{matrix}$, is formed when the imide is warmed with aqueous sodium carbonate. It crystallises in transparent, prismatic needles, and melts at 97—98°. The free acid corresponding with the anhydride cannot be obtained, but its salts are formed by dissolving the anhydride in boiling alkalis or alcoholic ammonia. The *ammonium salt*, $C_{12}H_{10}O_5(NH_4)_2$, melts at 144—146°, and the *sodium* and *barium* salts are both crystalline. Fuming hydriodic acid at 165° converts the anhydride into phenylsuccinic acid, which is a crystalline powder melting at 160—161° (stated by Spiegel as 167°).

The formation of phenylamidomaleïnimide from the ethereal salts of pulvic acid can best be explained by adopting Spiegel's view, that this acid is a hydroxy-lactone. A. H.

Thio-derivatives of β-Naphthol. By R. Henriques (*Ber.*, 1894, **27**, 2993—3005).—By the action of sulphur chloride on β-naphthol in

chloroform solution, *di-β-hydroxydinaphthylic sulphide*, $S(C_{10}H_6{\cdot}OH)_2$, is formed; it is sparingly soluble in chloroform and in carbon bisulphide, and separates in long, silky needles, or in colourless, transparent, highly lustrous, round crystals, and melts at 211°. With concentrated sulphuric acid, a bluish-green coloration is produced; with diazo-derivatives, sulphur is eliminated, and the ordinary azo-naphthol dyes are produced; the sulphur is not, however, removed by treatment with silver salts. The molecular weight was determined by the boiling point method. The compound is identical with that (m. p. 214°) prepared by Dahl and Co. by heating β-naphthol, sulphur, and lead oxide at 180—200°, and with the compound (m. p. 210°) obtained by Lange (Abstr., 1888, 375) by heating naphthol with sulphur in alkaline solution, and to which he erroneously gives the formula $S_2(C_{10}H_6{\cdot}OH)_2$. The *lead salt*, $C_{20}H_{12}SO_2Pb$, is yellow and amorphous; the *acetyl* derivative, $S(C_{10}H_6{\cdot}OAc)_2$, crystallises in colourless needles, and melts at 193°.

Dithiodi-β-hydroxydinaphthylic bisulphide, $\begin{matrix} S{:}S{\cdot}C_{10}H_6{\cdot}OH \\ | \\ S{:}S{\cdot}C_{10}H_6{\cdot}OH \end{matrix}$ or

$$OH{\cdot}C_{10}H_6{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}C_{10}H_6{\cdot}OH,$$

is formed, together with the sulphide, from which it is separated by means of its greater solubility in carbon bisulphide, and is deposited in large, sulphur-coloured crystals, melting at 141°; the yield is 15 per cent. of the naphthol employed. The compound is also formed by heating dihydroxydinaphthylic bisulphide (see below) with sulphur in alkaline solution; it is decomposed by silver salts, silver sulphide being precipitated, and dissolves in alkalis with an intense, yellow colour. The *lead salt*, $C_{20}H_{12}S_4O_2Pb$, is orange coloured; the *acetyl* derivative, $C_{20}H_{12}S_4O_2Ac_2$, crystallises in pale yellow needles, melting at 164°.

Di-β-hydroxydinaphthylic bisulphide, $S_2(C_{10}H_6{\cdot}OH)_2$, is separated by means of its lead salt from the chloroform mother liquors obtained in the preparation of the preceding dithio-compound and sulphide; it readily dissolves in all organic solvents, in alkali carbonates, and in borax solutions, and crystallises in yellow needles, melting at 166°; it is decomposed by silver salts. The *lead salt*, $C_{20}H_{12}S_2O_2Pb$, is orange coloured; the *acetyl* derivative resembles that of the preceding compound, and melts at 194°.

Dithiodihydroxydinaphthylic bisulphide and dihydroxydinaphthylic bisulphide give with potassium ferricyanide pale yellow, sparingly soluble ferricyanides; dihydroxydinaphthylic sulphide, in the same circumstances, is oxidised to *dehydrodioxydinaphthylic sulphide*, $C_{20}H_{12}SO_2$, which is deposited in large, red crystals, melting at 155°. The compound contains no hydroxyl, it dissolves in concentrated sulphuric acid with a dark blue colour, and readily reacts with hydroxylamine, although the products could not be isolated. The *phenylhydrazide*, $S(C_{10}H_6{\cdot}N_2HPh)_2$, crystallises in brick-red needles, melting at 184°.

Isodihydroxydinaphthylic sulphide is prepared by the reduction of the preceding compound with zinc dust and glacial acetic acid; it crystallises in long, pale yellow needles, melts at 152°, is readily

soluble, and is easily converted into dihydroxydinaphthylic sulphide by heating with alkalis. With potassium ferricyanide, the dehydro-derivative is regenerated; by the action of diazo-compounds, azo-naphthols are formed and sulphur eliminated. The *silver salt* is colourless; the *lead salt*, $C_{20}H_{12}SO_2Pb$, resembles that of the isomeric compound; the *acetyl derivative* is crystalline, and melts at 147—148°.

Dinaphthylenethiophen, $C_{20}H_{12}S$, is prepared by the action of concentrated sulphuric acid on isodihydroxydinaphthylic sulphide at 100°, the sulphate dissolving with a blue-green colour, and evolution of sulphurous anhydride; the compound crystallises from glacial acetic acid in yellow needles, melts at 147°, is neutral, and boils without decomposing; the coloration produced with sulphuric acid is similar to that of the original sulphide. The yield is 60 per cent. of the sulphide employed. Dihydroxydinaphthylic sulphide gives no thiophen derivative. The author discusses in detail the constitution of dehydrodioxydinaphthylic sulphide and of isodihydroxydinaphthylic sulphide; the former, although generally resembling the quinones, differs from them in its behaviour towards phenylhydrazine and reducing agents; he considers that the two dihydroxydinaphthylic sulphides are stereoisomeric,

Normal (anti-) sulphide (m. p. 211°).

Iso- (syn-) sulphide (m. p. 152°).

this is in complete accord with their behaviour, and, if correct, is the first example of simple stereoisomeric sulphur compounds. The dehydro-derivative and the thiophen probably have the formulæ $C_{10}H_6<\overset{S}{O}>C_{10}H_6$ [S : O = 1 : 2] and $C_{10}H_6<\overset{}{\underset{S}{\diagdown\diagup}}>C_{10}H_6$ respectively.

J. B. T.

Preparation of 1 : 2-Naphthaquinone. By K. Lagodzinski and D. Hardine (*Ber.*, 1894, **27**, 3075—3076).—An improvement of the method of Stenhouse and Groves (this Journal, 1877, ii, 52). Fifty grams of 2-naphthol is dissolved in a solution of 14 grams of sodium hydroxide in 500 c.c. of water. The whole is then placed in a 3-litre vessel, diluted with 1 litre of water, and stirred with 25 grams of sodium nitrite; a large lump of ice (about 500 grams) is then added, and the stirring continued while 700 c.c. of 10 per cent. sulphuric acid is gradually added. After 2—3 hours, the precipitate is collected on a calico filter and washed with water until the washings have only a feebly acid reaction. It is then placed in a 1½-litre flask, 300 c.c. of 10 per cent. sodium hydroxide added, and the whole diluted with water to 1,200 c.c., and warmed for a time on the water bath. Hydrogen sulphide is passed through the warm solution until white crystals of amidonaphthol begin to separate. These are collected on a porcelain funnel, washed with water, treated with 700 c.c.

of 5 per cent. sulphuric acid previously warmed to 70—80°, and filtered through a folded filter; the residual sulphur is washed with another 700 c.c. of the acid, and the united filtrates are cooled with a large lump of ice and oxidised with potassium dichromate. The 1 : 2-naphthoquinone, which then separates out in orange-yellow needles, is carefully washed until free from sulphuric acid. The yield is 47·5 grams, 86·6 per cent. of the theoretical. C. F. B.

Derivatives of α-Naphthylamine. By C. Böttinger (*Chem. Zeit.*, 1894, **18**, 483—484).—*Dichloracet-α-naphthalide* is prepared by moderately warming a mixture of dichloracetic acid and α-naphthylamine; it separates from ether in colourless crystals, and melts at 164°. *Glyceric-α-naphthalide* is obtained by warming α-naphthylamine with an alcoholic solution of glyceric acid; it is crystalline, and melts at 137°; a secondary product (m. p. 214°) was also isolated in small amount. Pyruvic acid reacts with α-naphthylamine in alcoholic solution, forming *pyruvic-α-naphthalide*, which melts at 148—149°. *α-Naphthylamine hydrogen tartrate* melts and decomposes at 180°; *tartaric-α-naphthalide* crystallises in long, white needles, and melts at 210°, and *α-naphthylamine citrate* crystallises in four-sided tablets, and melts at 146°. The citrate and tartrate of α-naphthylamine have a burning taste. A. R. L.

α-Dinaphthalidocitric acid. By C. Böttinger (*Chem. Zeit.*, 1894, **18**, 672).—Of the two theoretically possible modifications of α-dinaphthalidocitric acid, one is obtained, together with other products, by heating a pulverised mixture of citric acid and α-naphthylamine at 140°; it crystallises from boiling alcohol in white needles, and melts at 187—188°. If dissolved in nitric acid of sp. gr. 1·48, a yellow nitro-compound is formed, which yields intensely reddish-yellow alkali salts. When the acid is treated with acetic anhydride, a yellow compound is obtained, which is insoluble in soda and is probably an anhydro-compound. The silver salt of α-dinaphthalidocitric acid is a white precipitate, insoluble in water, and very stable. A. R. L.

1 : 2-Amidonaphtholsulphonic acids. By M. Böniger (*Ber.*, 1894, **27**, 3050—3054).—1 : 2 : 2′-Nitrosodihydroxynaphthalene, when heated with sodium hydrogen sulphite and hydrochloric acid, yields, by a reaction already described (Abstr., 1894, i, 199), 1 : 2 : 2′-*amidodihydroxynaphthalene-4-sulphonic acid*; this can be oxidised with nitrous acid to 2′-*hydroxy*-1 : 2-*naphthaquinone-4-sulphonic acid*, and this, with aniline, yields 2 : 2′-*dihydroxy-4-anilidonaphthaquinone*. 1 : 2 : 3-Nitrosohydroxynaphthalenesulphonic acid and 1 : 2 : 2′-nitrosohydroxynaphthalenesulphonic acid undergo an analogous series of reactions. C. F. B.

Nomenclature of Cyclic Derivatives of Naphthalene. By C. Graebe (*Ber.*, 1894, **27**, 3066—3068).—It is proposed that when, in compounds of the type of carbazole or anthracene, one phenylene group is replaced by naphthylene, the term "Naphtho-" (or

"Naphth-") should be prefixed to the name of the parent substance; and that when both the phenylene groups are replaced by two naphthylene groups, the term "Dinaphtho" should be prefixed. Thus the compound $C_{10}H_6<\overset{CO}{\underset{O}{}}>C_6H_4$ would be termed *naphthoxanthone*, the compound $C_{10}H_6<\overset{CO}{\underset{O}{}}>C_{10}H_6$, *dinaphthoxanthone*.

C. F. B.

1 : 2-Dihydroxynaphtho-3 : 4-Acridone. By K. Lagodzinski and D. Hardine (*Ber.*, 1894, **27**, 3068—3075).—When 1 : 2-naphthaquinone is dissolved in acetic acid and the solution warmed with anthranilic acid, 2-*hydroxynaphthaquinone-4-anilido-orthocarboxylic acid*, $C_{10}H_5O(OH):N\cdot C_6H_4\cdot COOH$ [O : OH : N = 1 : 2 : 4], is formed. This crystallises in dark red plates with a metallic lustre, and melts at 270—271°; it yields no anhydride (acridone), but is hydrolysed by dilute mineral acids to 2-hydroxynaphthaquinone and anthranilic acid.

If a solution of anthranilic acid in water and alcohol is warmed with aqueous potassium 1 : 2-naphthaquinone-4-sulphonate, 1 : 2-*naphthaquinone-4-anthranilic acid*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot COOH$ [O_2 : NH = 1 : 2 : 4], isomeric with the preceding compound, is formed. This crystallises in dark red needles, and melts at 252°; its *methylic salt* forms brilliant, dark red crystals, which melt at 188°. When heated with strong sulphuric acid at 200°, it yields 1 : 2-*naphthaquinone-3 : 4-acridone*, $C_{10}H_4O_2<\overset{CO}{\underset{HN}{}}>C_6H_4$, which crystallises in reddish-yellow needles, and melts above 400°. With orthophenylenediamine it yields a dark yellow *azine*, which melts at 276°, and it can be readily hydrolysed to hydroxynaphthaquinone and anthranilic acid. When suspended in acetic acid and reduced with sulphurous anhydride, it yields brown, crystalline 1 : 2-*dihydroxy-3 : 4-naphthacridone*, $C_{10}H_4(OH)_2<\overset{CO}{\underset{NH}{}}>C_6H_4$; this is not, like alizarin, a stable substance, nor does it dye with mordants; it has rather the properties of a quinol-derivative, being oxidisable with extreme readiness to the corresponding quinone; its yellow *diacetyl derivative* melts at 280°.

C. F. B.

Dihydrophenonaphthacridine and Phenonaphthacridine. By M. Schöpff (*Ber.*, 1894, **27**, 2840—2845; compare Abstr., 1894, i, 41).—*Dihydrophenonaphthacridine*, $C_{10}H_6<\overset{CH_2}{\underset{NH}{}}>C_6H_4$, has been already described as phenonaphthacridine (*loc. cit.*); the *acetyl* derivative melts at 181—181·5°.

Phenonaphthacridine, $C_{10}H_6<\overset{CH}{\underset{N}{}}>C_6H_4$, is obtained by oxidising the dihydro-derivative with silver nitrate; it melts at 225—226°. The *hydrochloride* and the *nitrate* crystallise in dark needles; the *platinochloride* forms minute, violet needles, and the *picrate* separates in brown needles. The *ethyl* derivative crystallises from alcohol in dark needles.

When phenonaphthacridone is reduced with sodium amalgam, the foregoing substance is formed in association with a red *substance*, which does not melt below 360°. If reduction is effected by means of zinc dust and acetic acid, the *hydroxydihydrophenonaphthacridine*, $C_{10}H_6<^{CH(OH)}_{NH}>C_6H_4$, which melts at 345°, is formed. It yields brown solutions with sulphuric acid and alcoholic potash, and is not dissolved by aqueous alkali. Reddish-brown fumes are evolved when the substance is heated, and a brown sublimate is formed, exhibiting the violet colour reaction of phenonaphthacridine with sulphuric acid.

M. O. F.

Analyses of Cotton Dyed with Alizarin. By C. Liebermann and P. Michaelis (*Ber.*, 1894, **27**, 3009—3019).—This work was undertaken in order to ascertain whether the theory of dyes advanced by Liebermann (Abstr., 1893, i, 370) is in accord with the facts so far as regards the relative proportions of base and dye present in the cloth. The theory has so far derived no support from the authors' observations.

Technically prepared samples of Turkey red, Bordeaux, and dark madder violet were examined, a detailed description of the analytical methods is given, and the results are tabulated. Specimens of cloth practically identical in appearance may contain totally different compounds; for example, the relative proportions of aluminium and tin in an aluminium-calcium-tin "lake," vary greatly, and the metals do not replace each other in atomic proportions. These results, and the somewhat contradictory analyses of other observers, are probably due to the presence of uncombined mordant in the cloth, which should, therefore, always be dyed to the deepest possible shade before being used for analysis.

J. B. T.

Some Points in Stereochemistry. By A. Combes (*Bull. Soc. Chim.*, 1894, [3], **11**, 261—263).—A criticism of Bouveault's recent paper (Abstr., 1894, i, 421). The author disputes (*a*) the novelty, and (*b*) the correctness of some of Bouveault's theories as to the relation between rotatory activity, and the constitution and stereoisomerism of cyclic compounds.

L. T. T.

Action of Camphoric Anhydride on Benzene in Presence of Aluminium Chloride. By E. Burcker and C. Stabil (*Compt. rend.*, 1894, **119**, 426—428).—The action of camphoric anhydride on benzene in presence of aluminium chloride, yields, as chief product, phenylcamphoric acid (Abstr., 1891, 324), and two others, which the authors have isolated. One of these, *phenylcamphoric anhydride*, $C_{16}H_{18}O_2$, is formed in quantity depending on the temperature, and is separated from the acid by means of its greater solubility in benzene. It is a yellowish, syrupy liquid, which does not crystallise even after remaining in a vacuum for three months.

The other product is formed when the action is violent and the substances remain in contact for a long time. It is a diphenyl compound, which has the composition $C_{22}H_{21}O_2$, and crystallises in reddish-yellow masses from benzene, in which it dissolves more

readily than phenylcamphoric acid. It may have the constitution $CHPr<^{CH_2\cdot CH_2}_{CH_2-CO}>CPh\cdot COPh$. C. H. B.

Natural Resins. By M. Bamberger (*Monatsh.*, 1894, **15**, 505—518; compare Abstr., 1892, 204).—The resin from *Pinus laricio* (Poir), which melts at about 100°, is resolved, on digestion with ether, into an α-modification (80 per cent.), which is soluble in ether, and a β-modification (20 per cent.), which is insoluble in ether. The *α-resin* is a reddish-white, amorphous powder, which is soluble in dilute potash, benzene, and toluene, and dissolves in concentrated sulphuric acid, forming a reddish solution; its methoxyl number is 33. The *β-resin* is a reddish-white powder, also soluble in dilute potash, but insoluble in benzene and toluene; it has a methoxyl number 62, and gives at first a green, and later a violet, coloration when hydrochloric acid is added to its alcoholic solution. When an excess of potash is added to an alcoholic solution of the α-resin, or of the crude resin, a colourless, crystalline, potassium compound is formed. A cold aqueous solution of the latter, when treated with hydrochloric acid, gives a powdery precipitate of *pinoresinol*, $C_{18}H_{18}O_6$, which gradually separates from its alcoholic solution in drusy masses, melts at 80—90°, contains two methoxyl groups, takes up 2 atoms of iodine, and furnishes the following derivatives.

The *potassium salt*, $C_{18}H_{16}O_6K_2 + 4H_2O$, is very soluble in water and methylic alcohol, but is insoluble in ethylic alcohol; the *calcium salt*, $C_{18}H_{16}O_6Ca$, is a white, insoluble precipitate; the *diacetyl-derivative*, $C_{18}H_{16}O_6Ac_2$, crystallises in slender, white needles, and melts at 164°; the *dibenzoyl*-derivative, $C_{18}H_{16}O_6Bz_2$, crystallises in short prisms, and melts at 160°. On treatment with methylic iodide, the potassium salt is converted into *dimethylpinoresinol*, $C_{18}H_{16}O_6Me_2$, which crystallises in scales and melts at 94°. The formula for pinoresinol must, therefore, be $C_{16}H_{10}O_2(OH)_2(OMe)_2$. The caffeïc and ferulic acids found in an earlier investigation (*loc. cit.*) are, in all probability, present in the resin in an uncombined state. G. T. M.

Scammony Resin. By H. Spirgatis (*Arch. Pharm.*, 1894, **232**, 482—486).—A reply to Poleck (Abstr., 1894, i, 471), maintaining the correctness of his former work, and especially of the analyses and proposed formula of barium scammonate. L. T. T.

Gaultherin, a New Glucoside from Betula Lenta. By A. Schneegans and J. E. Gerock (*Arch. Pharm.*, 1894, **232**, 437—444).—In 1844, W. Procter, jun., announced (*Amer. J. Pharm.*, N.S., **15**, 249) the existence, in the bark of *Betula lenta*, of a glucoside, to which he gave the name gaultherin; he did not, however, obtain it in the pure state, and the authors have therefore re-examined the *Betula lenta* bark. In extracting the bark, it was found that even with 94 per cent. alcohol partial hydrolysis of the glucoside took place, the odour of methylic salicylate becoming apparent. By using for extraction a solution of lead acetate (15 per cent. of the weight of the bark) in strong alcohol, this decomposition was pre-

vented. *Gaultherin*, $C_{14}H_{18}O_8 + H_2O$, crystallises in colourless needles, which are easily soluble in glacial acetic acid and in alcohol, slowly but freely in water, and almost insoluble in ether, chloroform, benzene, and acetone. The aqueous solution does not affect iron salts, nor does it affect Fehling's solution in the cold, but at 100° cuprous oxide is at once precipitated. Strong sulphuric acid dissolves the glucoside, forming a pale red solution, which rapidly darkens and decomposes. When the dry glucoside is heated, the odour of methylic salicylate becomes apparent at about 100°, and the substance blackens and decomposes at 120°. The aqueous solution has a bitter taste and is levorotatory. The glucoside is decomposed by mineral acids, by alkalis, or by heating the aqueous solution at 130—140°, yielding a carbohydrate and methylic salicylate. L. T. T.

Crystalline Constituents of True Coto Bark. By O. Hesse (*Annalen*, 1894, **282**, 191—207; compare Abstr., 1894, i, 380).—The coto bark employed by Jobst and Hesse (Abstr., 1880, 325) was derived from Bolivia, whilst nowadays the term has been extended to include varieties from Venezuela and Brazil. The following results were obtained with the bark from Bolivia.

Cotoïn extracted from this bark is identical with that obtained from other varieties. *Benzoylcotoïn* is formed by the direct action of benzoic anhydride, and crystallises in compact lustrous prisms, melting at 110—112°. It gives a brownish-red coloration with ferric chloride. *Dibenzoylcotoïn* is best prepared by the action of benzoic chloride on cotoïn, and crystallises in concentric groups of small needles, melting at 134—135°. Hydrocotoïn only yields one *benzoyl*-derivative, which crystallises in white needles, melts at 113°, and gives no coloration with ferric chloride.

The substance known as dicotoïn has the formula $C_{25}H_{20}O_6$, and not $C_{44}H_{34}O_{11}$ as formerly supposed. The cryoscopic determination of the molecular weight, however, gives the number 214, instead of 416, as required by the above formula. This is explained by the fact that dicotoïn is in reality a mixture of cotoïn with a substance which has the composition and molecular weight corresponding with the formula $C_{11}H_8O_2$, and may be obtained from dicotoïn by adding ferric chloride to its alcoholic solution and evaporating. The iron compound of cotoïn is thus formed, whilst the new substance crystallises out in long needles. It separates from light petroleum in colourless, strongly lustrous plates, melts at 60—61°, and volatilises at a higher temperature. It does not contain the hydroxy-group, and gives no coloration with ferric chloride. With phenylhydrazine, it forms a compound of the formula $C_{23}H_{22}N_4O$, which crystallises in colourless needles, melting at 194°. In all its properties, it bears a very close resemblance to phenylcoumalin; as, however, the latter melts at 68°, the identity of the two cannot be considered as proved.

Pseudodicotoïn, $C_{25}H_{20}O_7$, is also a mixture of cotoïn with a substance of the formula $C_{11}H_8O_3$, which the author terms *hydroxyphenylcoumalin;* this crystallises from light petroleum in colourless plates or white needles, and melts at 61°. Acetic anhydride converts it into *acetoxyphenylcoumalin*, $C_{11}H_7AcO_3$, which crystallises in

lustrous needles and melts at 65°. With phenylhydrazine, it forms a compound, $C_{23}H_{22}N_4O_3$, crystallising in flat needles and melting at 193°. When treated with aqueous potash, it is converted into *β-phenylcoumalic acid*, $C_{11}H_{10}O_3$, which crystallises from acetic acid in prisms or plates and melts at 207°. The melting point is, however, uncertain, as the acid passes gradually into its lactone, which melts at 221°.

The paracotoïn obtained from the specimens in question agreed in properties with that previously described. The author confirms the occurrence of piperonylic acid among the products obtained by fusing paracotoïn with potash (Ciamician and Silber, Abstr., 1894, i, 51).

A. H.

Properties of the Dihydroquinolines, and the Constitution of Ring Systems containing Nitrogen. By G. Ciamician (*Ber.*, 1894, **27**, 3077—3081).—It has already been shown by Ferratini (Abstr., 1893, i, 602) that the trimethyldihydroquinoline obtained by the action of methylic iodide on 2′-methylindole, which has one of the following formulæ, $C_6H_4<\begin{matrix}CMe{:}CH\\ |\\ NMe{\cdot}CHMe\end{matrix}$, or $C_6H_4<\begin{matrix}CHMe{\cdot}CH\\ ||\\ NMe{-}CMe\end{matrix}$, has properties which strongly resemble those of the indoles, although it may be readily converted into quinoline derivatives. The author finds further that when the hydriodide of dihydrotrimethylquinoline is heated, it loses methylic iodide and is converted into trimethylindole, the yield of the latter being very satisfactory. The action is analogous to that which takes place when the hydriodides of tertiary bases are heated, methylic iodide and the corresponding secondary base being obtained.

The great similarity in the properties of the two series is readily explained by the above formulæ of the dihydroquinoline derivatives and the usual formula of the indole ring, the former being "nuclear" homologues of the latter. Bamberger's centric formulæ with a quinquavalent nitrogen atom do not, however, afford a ready explanation of the analogy.

H. G. C.

Ethereal Salts and Betaïnes of Quinolinesulphonic acids. By A. Claus and J. Steinitz (*Annalen*, 1894, **282**, 130—138; compare the next abstract).—*Methylic quinoline*-1-*sulphonate*,

$$C_9NH_6SO_3Me,$$

is obtained by the action of methylic iodide on the silver salt at 85°, and crystallises in colourless, lustrous prisms melting at 96°. It gradually decomposes when kept, with formation of the free acid and a volatile oil, which has not yet been analysed; this decomposition proceeds much more rapidly at 100°. The *benzylic salt* crystallises in splendid, six-sided tablets and prisms, which have a diamond lustre, and melt at 84°. When heated at 200°, it decomposes with formation of the free acid and an oil, which has the empirical formula $C_{14}H_{13}$. These two salts and the ethylic salt do not appear to form a methiodide, and it has therefore been found impossible to prepare the corresponding betaïnes.

Quinoline-4-sulphonic acid methylbetaïne, $C_9NH_6MeSO_2$, is readily formed, and crystallises in yellowish prisms, which can be heated to 360° without undergoing any change. It dissolves in alkalis, but cannot be recovered, either free or in the form of a salt, by acidifying the solution. The betaïne, moreover, does not combine with alkylic iodides.

Similar results were obtained with *quinoline-3-sulphonic acid methylbetaïne*, which may be prepared from the silver salt and methylic iodide at 100°.

The systematic investigation of this action has shown that many of the monobromo-derivatives of the 4- and 3-sulphonic acids only yield ethereal salts when their salts are heated with methylic iodide, whilst others, such as the 3-bromo- and 3-chloro-4-sulphonic acids only yield betaïnes. A. H.

Alkyl Derivatives of Quinaldine-β-carboxylic acid. By A. Claus and J. Steinitz (*Annalen*, 1894, **282**, 107—130; compare Abstr., 1893, i, 728). — Ethylic quinaldine-β-carboxylate methiodide, $C_9NH_5Me{\cdot}COOEt,MeI$, has been described by Hantzsch (Abstr., 1886, 369). The *methochloride* crystallises in long, colourless needles, melting at 158°. The behaviour of these compounds towards alkalis has already been described by Hantzsch. The authors find that the insoluble amorphous yellow substance finally obtained has the composition $C_{13}NH_{13}O_2{:}CH_2$, but it is probably a polymeride.

Ethylic quinaldinecarboxylate ethiodide is formed with considerable difficulty, and crystallises in groups of plates which melt and decompose at 236°. The *ethochloride* forms well-developed prisms, and melts at 146°; its *platinochloride*, $(C_{13}H_{13}O_2N,EtCl)_2PtCl_4$, crystallises in compact, red prisms, and melts and decomposes at 238°.

Ethylic ethylidenequinaldinium-β-carboxylate, $C_{13}NH_{13}O_2{:}CHMe$, is obtained as an amorphous, yellowish-red mass, which has not been analysed, by the action of alkalis on the ethiodide. It is completely soluble in ether, and does not undergo polymerisation to an insoluble compound when kept. On treatment with hydrochloric acid, it yields the ethochloride melting at 146°. The *silver salt* of quinaldine-β-carboxylic acid is a micro-crystalline powder, and when treated with methylic iodide yields the *methylic salt* of the acid. This substance can also be obtained by synthesis from methylic acetoacetate and orthamidobenzaldehyde, and by the action of methylic iodide on quinaldinecarboxylic acid; in the latter case, the direct product is the hydriodide of the methylic salt. The methylic salt forms colourless needles, melting at 72°.

The following additive compounds and ethereal salts of quinaldine-β-carboxylic acid have also been prepared. From the methylic salt, the *methiodide*, vitreous, yellow prisms, melting at 200°; the *methochloride*, colourless, vitreous prisms, melting at 157°; the *ethiodide*, lemon-yellow plates, melting at 210°; the *ethochloride*, colourless, vitreous needles, melting at 150°; and the *ethobromide*, granular crystals, melting at 154°. From the ethylic salt, the *ethobromide*, granular crystals, melting at 217°. The *propylic salt* forms colourless,

vitreous prisms, and melts at 51°; the *propylic methiodide* golden-yellow needles, melting at 186°; the *benzylic salt* forms colourless prisms, melting at 82°, and the *benzylic methiodide* flat, golden-yellow needles, melting at 172°.

The methylic methochloride and iodide, when treated with alkalis, yield a yellow, amorphous substance which behaves in a similar manner to the corresponding derivative of the ethylic salt. It is a yellow powder, melts and decomposes at 182°, and has the formula of *methylic methylenequinaldinium-β-carboxylate*,

$$C_9NH_5Me(COOMe):CH_2,$$

of which it is probably a polymeride.

Quinaldine-β-carboxylic acid differs from the γ-carboxylic acids of the quinoline series in two important respects. It forms no direct additive compounds with halogen alkyls without at the same time being converted into an ethereal salt, and the additive compounds of the ethereal salts do not yield the corresponding betaïne when treated with alkalis.

Quinaldine-β-carboxylic acid methochloride can, however, be readily obtained by heating the methochloride of one of the ethereal salts with fuming hydrochloric acid. It forms short, vitreous prisms, and melts with decomposition at 230°. The corresponding *betaïne* forms thick, monosymmetric prisms containing $2H_2O$, which are lost at 100°, the anhydrous compound melting at 144°. It has an intensely bitter taste, and is readily decomposed with formation of a violet colouring matter. It unites readily with methylic and ethylic iodides to form compounds which are in every respect identical with the methylic methiodide and ethylic methiodide already described. This behaviour confirms the view expressed by Claus and Büttner (Abstr., 1893, i, 731) as to the course of the analogous reaction with α-phenylcinchoninic acid.

The betaïne dissolves in alkalis, forming a salt which could not be isolated, and does not form an oxinic acid. A. H.

4′-Orthohydroxyphenylquinoline and 4′-Metahydroxyphenylquinoline. By E. Besthorn, E. Banzhaf, and G. Jaeglé (*Ber.*, 1894, **27**, 3035—3043).—*Orthoethoxyacetophenone* was prepared from ethylic ethylsalicylate by Tahara's method (Abstr., 1892, 844); it melts at 43°, and boils at 243—244°. It was converted, by the same method as that used in the case of the para-compound (Abstr., 1894, i, 344), into *orthoethoxybenzoylacetone*,

$$OEt\cdot C_6H_4\cdot CO\cdot CH_2\cdot CMeO;$$

this melts at 58°, and forms a *sodium salt*, which, when warmed with aniline and acetic acid, yields a yellow *anilide*,

$$OEt\cdot C_6H_4\cdot CO\cdot CH_2\cdot CMe:NPh.$$

When the latter is heated at 50° with sulphuric acid monohydrate, several reactions take place, and as a result of one of these some 4′-*orthoethoxyphenylquinaldinesulphonic acid*, $OEt\cdot C_6H_3(SO_3H)\cdot C_{10}NH_8$, is formed, and crystallises in tiny, white needles. When this is boiled with hydrobromic acid, it is converted into 4′-*orthohydroxyphenyl-*

quinaldine, $OH \cdot C_6H_4 \cdot C_{10}H_8N$, which melts at about 187—188°; and its sodium salt. when heated with benzaldehyde and zinc chloride at 200°, yields a *benzylidene compound*, $OEt \cdot C_6H_3(SO_3H) \cdot C_{10}H_6N{:}CHPh$. If the latter is oxidised with permanganate, and the product heated with hydrobromic acid, yellowish-red *4′-orthohydroxyphenylquinaldinic acid*, $OH \cdot C_6H_4 \cdot C_9NH_5 \cdot COOH$, is formed; this melts and decomposes at 243—245°, and, when heated at 250°, yields *4′-orthohydroxyphenyl quinoline*, $OH \cdot C_6H_4 \cdot C_9NH_6$, identical with the "quinolinephenol" obtained by Koenigs from apocinchene (Abstr., 1893, i, 377).

Metamethoxyacetophenone was prepared like the para-compound (Abstr., 1894, i, 344); it boils at 239—241°. *Metamethoxybenzoylacetone* was obtained as an oil, its *anilide* as yellow needles melting at 84—85°. This anilide yields a sulphonic acid, the barium salt of which forms a *benzylidene* compound. From the latter *4′-metahydroxyphenylquinaldinic acid* can be obtained; this melts and decomposes at about 235°, yielding *4′-metahydroxyphenylquinoline*, identical with the Py-3-β-phenolquinoline of Koenigs and Nef (Abstr., 1887, 599).

C. F. B.

Paramethoxy-α-phenylcinchoninic acid, Parahydroxycinchoninic acid, and Parahydroxy-α-phenylcinchonine. By A. Claus and G. Brandt (*Annalen*, 1894, **282**, 85—107).—*3-Methoxy-2′-phenylcinchoninic acid methiodide*, $OMe \cdot C_9NH_4Ph \cdot COOH,MeI$, is obtained by heating α-phenylquininic acid with methylic iodide at 135—136°, and forms aggregates of small, reddish-yellow needles, melting at 216°. The *methochloride* is prepared by triturating the methiodide with moist silver chloride, and is a hygroscopic mass, which crystallises from alcohol in small needles, melting at 195°. The corresponding *betaïne* is formed when the methiodide is treated with moist silver oxide, and crystallises with $1H_2O$ in yellow, vitreous prisms, which become anhydrous at 100° and melt at 218°. The betaïne is also formed when the aqueous solutions of the methochloride and iodide are boiled, and when these substances are treated with alkalis. The further action of alkali produces a quaternary ammonium hydroxide of the formula $OMe \cdot C_9NH_4Ph \cdot COOH,MeOH$, from which the original betaïne, or one of its salts, can readily be regained by acidification of its solution. This substance, probably owing to the presence of the phenylic group, is much more stable than the corresponding derivative of quininic or cinchoninic acid, and does not form an oxinic acid.

It was found impossible to prepare an ethobromide of the acid. The *sodium salt* of methoxyphenylcinchoninic acid forms slender, yellow needles, containing $6H_2O$, whilst the *copper salt* is a light green precipitate. The *hydrochloride*, $C_{17}H_{13}O_3N + 3HCl$, crystallises from concentrated hydrochloric acid in lemon-yellow, vitreous needles, and loses 2HCl at 100°.

3-Hydroxycinchoninic acid methiodide, $OH \cdot C_9NH_5 \cdot COOH,MeI$, is formed from its components with considerable difficulty, and crystallises from alcohol in splendid, orange-yellow, vitreous prisms, melting at 302°. Its solution in water readily decomposes, with formation of resinous compounds. The *methochloride* may be prepared by the action of silver chloride, but is best obtained by heating

the methochloride of quininic acid with fuming hydrochloric acid at 230°, this being a reaction capable of general application to this class of substances. It forms flat, green crystals, and melts at 295°. The corresponding *betaïne* is formed by the action of water, alkalis, or silver oxide on the foregoing compounds, and crystallises with $1H_2O$ in large tablets or prisms, which lose their water at 100° and melt at 304°. The product of the action of alkalis on the betaïne, *methylquinoliniumhydroxidecarboxylic acid*, has not been isolated. Its solution is stable in the air, so that the presence of the free hydroxy-group has the same influence on the stability of the compound as has the phenylic group in the case of methoxyphenylcinchoninic acid.

3-*Hydroxy-2′-phenylcinchoninic acid*, $OH{\cdot}C_9NH_4Ph{\cdot}COOH$, may be prepared, by Döbner's method, from parahydroxyaniline, pyruvic acid, and benzaldehyde, and forms small, vitreous plates and needles, which decompose at 295—300°. Its alkaline solutions become dark brown on exposure to the air. The *copper* and *silver* salts are amorphous precipitates. The *methochloride* is prepared by the action of hydrochloric acid at 230—235° on the methochloride of methoxyphenylcinchoninic acid, and forms greenish-yellow, lustrous plates, melting at 248°. The *methiodide* can only be obtained with great difficulty from its components and is very unstable. The *betaïne* forms almost colourless, granular crystals, and melts at 243°. The alkaline solutions of the betaïne are somewhat unstable, but no compound of the nature of an oxinic acid is formed, resinous matter being gradually produced.

The solubility of the substituted cinchoninic acids is shown in the following table. 100 grams of the boiling saturated solution contains

Paramethoxycinchoninic acid	1·24 grams.
Paramethoxy-α-phenylcinchoninic acid ...	2·22 „
Parahydroxycinchoninic acid.....	0·28 gram.
Parahydroxy-α-phenylcinchoninic acid ...	0·44 „

A number of ethereal salts have also been prepared by the action of an alkylic iodide on the silver salt of the acid.

	Methylic salts. M. p.	Ethylic salt. M. p.
2′-Phenylcinchoninic acid	61°	—
3-Methoxycinchoninic acid	85	—
3-Methoxy-2′-phenylcinchoninic acid ..	111	105°
3-Hydroxy-2′-phenylcinchoninic acid ..	148	—

These salts readily undergo decomposition when heated, the free acid being formed, together with a terpene-like substance, the nature of which has not yet been determined. A. H

Pure Dextrorotatory Coniine. By A. Ladenburg (*Ber.*, 1894, **27**, 3063—3066).—Coniine was prepared synthetically in the same way as before, but on a larger scale; 30 grams of inactive coniine, boiling at 165—169°, were obtained. This was treated with dextro-

rotatory tartaric acid, as before, when the salt of dextrorotatory coniine crystallised out. This was, however, now recrystallised three times, after which it yielded a coniine, boiling at 167·7° (corr.), and with sp. gr. = 0·8438 and specific rotation $[\alpha]_D = +18·3°$, both at 23°. The difference between this and the earlier numbers is attributed to the presence of isoconiine in the sample then investigated.

C. F. B.

Nicotine (Metanicotine). By A. Pinner (*Ber.*, 1894, **27**, 2861—2869; compare Abstr., 1894, i, 388).—When the additive compound of benzoic chloride and nicotine is heated with strong hydrochloric acid at 100°, benzoic acid and nicotine are formed, whilst, if boiled with sodium ethoxide, hydrogen chloride is eliminated and benzoylmetanicotine is produced. *Acetylmetanicotine* is obtained by heating nicotine with acetic anhydride for 10—12 hours at 170°; it is hydrolysed only with difficulty, yielding metanicotine. When metanicotine is heated with a strong solution of barium hydroxide for 10—12 hours at 170°, methylamine is formed, together with a *base*, C_9H_9N, of which the *picrate* melts at 151°.

The action of bromine on metanicotine gives rise to the *compound*, $C_{10}H_{14}Br_2N_2,2HBr,Br_2$, crystallising in reddish-yellow needles, which melt at 170°. On adding dilute caustic soda to the hydrobromide of metanicotine bromide, *monobromometanicotine*, $C_{10}H_{13}BrN_2$, separates in the form of an oil; the *picrate* melts at 190°. Reduction with hydrochloric acid and zinc dust gives rise to the formation of metanicotine.

The optical activity of cotinine, dibromocotinine, and dibromoticonine has been determined. The first-named has $[\alpha]_D = -56°$, whilst dibromocotinine has $[\alpha]_D = +95·5°$, and dibromoticonine has $[\alpha]_D = +13·6°$; the determinations were made at 20°.

M. O. F.

Derivatives of Caffeïne. By L. Crämer (*Ber.*, 1894, **27**, 3089—3092).—*Methylamidocaffeïne*, $C_8H_9N_4O_2·NHMe$, is readily obtained in a similar manner to amidocaffeïne by heating chlorocaffeïne with methylamine and alcohol at 100°; it crystallises from hot water in slender, colourless needles, melts at 310—315°, simultaneously becoming brown. The *picrate* crystallises in yellow plates. *Ethylamidocaffeïne*, $C_8H_9N_4O_2·NHEt$, is prepared in a similar manner, and also forms slender needles, melting at 226—230° with partial sublimation.

Hydrazidocaffeïne, $C_8H_9N_4O_2·N_2H_3$, prepared by boiling chlorocaffeïne with an aqueous solution of hydrazine hydrate, crystallises in slender, colourless needles, melting and completely decomposing at 240°. It reduces Fehling's solution on warming, and yields a *hydrochloride*, which crystallises well and dissolves readily in warm water. With benzaldehyde, the hydrazine compound forms *benzylidenehydrazidocaffeïne*, $C_8H_9N_4O_2·N_2H:CHPh$; this crystallises in slender needles, melting at 270° to a brown liquid. On treatment with nitrous acid, it is converted into *azimidocaffeïne*, $C_8H_9N_4O_2N_3$, which forms colourless needles, sparingly soluble in water, and rapidly becomes red in the air when moist.

Anilidocaffeïne, $C_8H_9N_4O_2·NHPh$, crystallises from alcohol in colour-

less needles, melting at about 260° and decomposing at a slightly higher temperature; the *hydrochloride*, $C_{14}H_{15}N_5O_2,HCl$, also crystallises in needles, which are dissociated by water. *Nitrosoanilidocaffeïne*, $C_8N_4H_9O_2{\cdot}NPh{\cdot}NO$, decomposes at about 225° and gives Liebermann's reaction. *Benzoylanilidocaffeïne*, $C_8N_4H_9O_2{\cdot}NPhBz$, is obtained by boiling anilidocaffeïne with benzoic chloride, and, after crystallisation from alcohol, melts at 225°. By the action of alcoholic potash on anilidocaffeïne at 120°, it is converted into *anilidocaffeïdine*, the sulphate of which crystallises well; the action of hydrochloric acid and potassium chlorate converts it into chloranil and dimethylalloxan. *Paratoluidocaffeïne* melts at 270—275°, *orthotoluidocaffeïne* at 230°, and *metaxylidocaffeïne* at 210—212°. H. G. C.

Thebaïne. By M. Freund (*Ber.*, 1894, **27**, 2961—2963).—Thebenine is not isomeric with thebaïne as Hesse thought, but contains hydroxyl in place of methoxyl, its *methiodide*, $C_{20}H_{24}NO_3I$, is crystalline, melts at 210°, and is resolved into trimethylamine and *thebenol*, $C_{17}H_{14}O$, on fusion with alkalis. Thebenol melts at 186°, and by distillation with zinc dust, or reduction with hydriodic acid and phosphorus, yields a hydrocarbon which melts at 135°, and is perhaps an ethylphenanthrene.

Thebenine ethiodide when fused with alkalis yields thebenol and methyldiethylamine, proving that thebenine is a secondary base. Thebaïne is a tertiary base, but its relationship to thebenine precludes the presence in it of the group NMe_2. When treated with alkalis, its methiodide yields tetramethylethylenediamine, not trimethylamine, as Roser stated; it is probable that dimethylhydroxyethylamine, which is closely related to morphine, is formed as intermediate product. The production of the ethylene base resembles that of tetrethylethylenediamine from triethylaminethylene iodide as observed by Ladenburg. The following provisional formulæ are given for thebaïne, thebenine, and thebenol respectively

$$C_{14}H_8(OMe)_2\begin{cases}NMe{\cdot}CH_2\\ O\text{—}CH_2\end{cases};\quad NHMe{\cdot}C_{14}H_7(OMe)(OH)\begin{cases}CH_2\\ O\end{cases}CH_2;$$

$$OMe{\cdot}C_{14}H_8(OH)\begin{cases}CH_2\\ O\end{cases}CH_2.$$

J. B. T.

Opium Alkaloïds. By O. Hesse (*Annalen*, 1894, **282**, 208—214).—When crude laudanine (*Annalen*, Suppl.-Bd., **8**, 272) is converted into the hydrochloride and this is recrystallised from water, the mother liquor is found to contain an alkaloïd, *laudanidine*, $C_{20}H_{25}NO_4$, which is isomeric with laudanine, but differs from it in being optically active ($[\alpha]_D = -87{\cdot}8°$). The new alkaloïd melts at 177° (laudanine melts at 166°), but in other properties closely resembles its isomeride. The *hydrochloride* is much more readily soluble in water than that of laudanine. The *hydriodide* is sparingly soluble, and the *platinochloride* is a brownish-yellow, amorphous mass. The *hydrogen oxalate* forms small, white needles. Acetic anhydride converts it into *acetyllaudanidine*, which crystallises with $1H_2O$, melts at about 98°, and dissolves in dilute aqueous potash and soda, but not in ammonia. It

seems probable that laudanine consists of two optically opposed constituents, of which laudanidine is one, but this question is being further investigated. A. H.

Benzoylquinine. By A. Wunsch (*Compt. rend.*, 1894, **119**, 407—409).—Schützenberger obtained benzoylquinine by the action of benzoic chloride on the alkaloïd, and described it as a resinous and uncrystallisable substance. The author prepares it by adding gradually, with frequent agitation, 60 parts of pure, well-dried, and finely-powdered quinine to 100 parts of benzoic chloride, heated on a water bath. The product, after cooling, is treated with several times its volume of cold water, which rapidly dissolves the benzoylquinine hydrochloride, but only very slowly attacks the excess of benzoic chloride. The base is purified by precipitation with ammonia and crystallisation from aqueous ether. It forms very distinct, highly refractive, colourless prisms of the composition

$$C_{20}H_{23}BzN_2O_2.$$

Benzoylquinine is insoluble in water, and the crystals remain unchanged even in contact with boiling water, but it dissolves readily in alcohol, benzene, chloroform, light petroleum, and carbon bisulphide, and also in ether, especially if it contains water. It crystallises from all the solvents except alcohol, and the crystals, which are anhydrous, melt at 139°, but decompose at a higher temperature.

Benzoylquinine is distinguished from quinine benzoate by its insolubility in water and its resistance to the action of potassium hydroxide. Like quinine, it yields a green coloration with chlorine water and ammonia, and the dilute aqueous solutions of its salts are fluorescent. It is neutral to both phenolphthaleïn and litmus, and even the basic salts are acid to litmus.

It forms two series of salts, namely, *basic salts*, which contain 1 mol. of the base and 1 mol. of a monobasic acid, and *normal salts*, which contain twice as much acid. The basic salts are very stable, and are insoluble, or almost insoluble, in water. They are usually hydrated, and effloresce rapidly. The normal salts are partially decomposed by water. The *basic hydrochloride* crystallises from alcohol in acicular prisms containing $\frac{1}{2}$ mol. H_2O, and is very soluble in alcohol; the *normal hydrochloride* crystallises from absolute alcohol in small, square prisms, which contain 1 mol. EtOH, absorb moisture rapidly from the air, and dissolve in all proportions in water and alcohol. The *basic salicylate* crystallises from dilute alcohol in anhydrous lamellæ; the *basic tartrate* forms brilliant needles containing $9H_2O$; the *basic succinate* forms colourless prisms, which contain $8H_2O$, and effloresce very rapidly. C. H. B.

Emetine. By H. Kunz-Krause (*Arch. Pharm.*, 1894, **232**, 466—481).—This paper is a continuation of the author's previous work (H. Kunz, Abstr., 1887, 980). Methylemetonium hydroxide (*loc. cit.*) has now been obtained as a golden-yellow, amorphous powder. Its solution is very strongly alkaline, and absorbs carbonic anhydride

from the air. The *carbonate* is an amorphous powder, softening at 120°, and melting with evolution of carbonic anhydride at 156—160°. *Ethylemetonium iodide*, $C_{30}H_{40}N_2O_5EtI$, crystallises in white needles; the *hydroxide* resembles the methyl base. Both these derivatives are quaternary ammonium bases.

In the preparation of emetine, a *colour base*, containing both nitrogen and sulphur, was found among the residues. The authors believe this to be an acetyl derivative of emetine, and by heating emetine with other acids, and with acetic and benzoic anhydrides, &c., they have obtained derivatives apparently analogous to it. This reaction is being further studied.

When emetine is heated with hydriodic acid, 4 mols. of methylic iodide are eliminated. Emetine therefore contains four methoxyl groups and almost certainly one hydroxyl group. The constitution of emetine may, therefore, be represented by the formula

$$C_{26}H_{27}N_2(OMe)_4{\cdot}OH,$$

and the nucleus $C_{26}H_{27}N$ probably contains one or more tertiary butyltoluene groups.

The author maintains the correctness of the above formula against Paul and Cownley's contention (Abstr., 1894, i, 155, and *Pharm. J. Trans.*, 1894, [3], **54**, 111), that emetine is a mixture of two alkaloïds, $C_{15}H_{22}NO_2$ and $C_{14}H_{20}NO_2$, and calls attention to the fact that each of these formulæ contains an uneven number of valencies.

Both methylemetine and the colour base resemble curare in their physiological action, producing paralysis of the motory system and then death. L. T. T.

Identity of Cytisine and Ulexine. By A. Partheil (*Arch. Pharm.*, **232**, 486—488).—The author maintains his claim to priority in proving the identity of these two alkaloïds.

The Products of Hydrolysis of Convolvulin, and its Composition. By H. J. Taverne (*Rec. Trav. Chim.*, 1894, **13**, 187—217).—Convolvulin, extracted by alcohol from jalap-root coming from Vera Cruz, was hydrolysed by dissolving it in baryta water, removing the barium with sulphuric acid, and boiling the solution with $\frac{1}{2}$ per cent. of free sulphuric acid. There were formed a volatile acid (methylethylacetic), a crystalline acid (hydroxypentadecylic) not volatile with steam, and a sugar which could not be obtained in the crystalline form, but which the author is nevertheless inclined to regard as glucose.

Methylethylacetic acid, CHMeEt·COOH, is identical with the substance obtained by Pagenstecher (Abstr., 1879, 455), except that it is optically active, having specific rotation $[\alpha]_D = +17° 30'$. *Hydroxypentadecylic acid*, $CHMeEt{\cdot}CH(OH){\cdot}C_9H_{18}{\cdot}COOH$, melts at 50·5° when pure; its *methylic salt* melts at 35°, and boils at 206—208° under 15 mm. pressure. When it is heated with phosphorus pentachloride and the product reduced with hydriodic acid and phosphorus, a *pentadecylic acid*, $C_{15}H_{30}O_2$, is obtained; this melts at 48°, and is isomeric, therefore, with the normal acid, which melts at 51°; it boils at 206°

under 14 mm. pressure. When the hydroxy-acid is oxidised with nitric acid, it yields methylethylacetic acid, and an *acid*, $C_{10}H_{18}O_4$, which melts at 116°, and boils at 235° under 13 mm., and at 294° under 100 mm. pressure; this acid is isomeric with sebacic acid, which melts at 133—133·5°

Possibly, convolvulin has the formula $C_{32}H_{62}O_{16}$, and its hydrolysis may then be represented by the equation

$$C_{32}H_{62}O_{16} + H_2O = 2C_6H_{12}O_6 + C_5H_{10}O_2 + C_{15}H_{30}O_3.$$

C. F. B.

Two Cactus Alkaloïds. By A. Heffter (*Ber.*, 1894, **27**, 2975—2979).—*Anhaline*, $C_{10}H_{17}NO$, is extracted from *Anhalonium fissuratum*; it crystallises in colourless, stellate prisms, and melts at 115°. The solution in concentrated sulphuric acid is colourless, even when warmed, but becomes green on the addition of a drop of nitric acid. The most characteristic reaction is the production of a yellow colour with nitric acid, changing to orange-red with potash. The *sulphate*, $(C_{10}H_{17}NO)_2,H_2SO_4 + 2H_2O$, crystallises in colourless, lustrous plates, and melts at 197°. The *hydrochloride*, $C_{10}H_{17}NO,HCl$, crystallises in slender, hygroscopic plates. The *oxalate* is anhydrous and resembles the sulphate. The yield of alkaloïd was very small, only 0·2 gram from 1 kilo. of the dry plant.

Pellotine, $C_{13}H_{21}NO_3$, so called from the Mexican name "pellote," of *Anhalonium Williamsi*, crystallises in colourless, transparent, anhydrous plates, and melts at 110°. The yield is 0·89 per cent. of the fresh plant. It dissolves in sulphuric acid with a slight yellow colour, changing to deep red with nitric acid. The *phosphotungstate* and *phosphomolybdate* are voluminous, the former white, the latter lemon coloured. The *potassiomercuric iodide* crystallises in pale yellow prisms; the *potassiocadmium iodide* in colourless, rectangular plates; the *potassiobismuth iodide* is amorphous at first, but changes to needles; the *iodopotassium iodide* crystallises in slender needles. The *picrate* crystallises in stellate prisms. The *platinochloride* is deposited in golden-yellow crystals; the *hydrochloride*, $C_{13}H_{21}NO_3,HCl$, in rhombic prisms. The *oxalate* crystallises in needles. The *methiodide*, $C_{13}H_{21}NO_3,MeI + H_2O$, is deposited in colourless prisms melting at 198°. The *methochloride*, $C_{13}H_{21},NO_3,MeCl$, crystallises in slender, colourless needles melting at 226°. Determinations by Zeisel's method show that pellotine contains two methoxy-groups. By the action of hydrochloric acid at 100°, methylic chloride is eliminated and a *base* formed in small quantity, which yields a *platinochloride* crystallising in orange-red prisms.

J. B. T.

Organic Chemistry.

Action of Reducing Agents on Metallic Cyanides: Compounds of Organic Bases with certain Metallic Salts. By F. REITZENSTEIN (*Annalen*, 1894, **282**, 267—280).—The author has investigated the red coloration which is developed on immersing a strip of zinc into a solution of potassium nickelocyanide containing ammonia and ammonium chloride (compare Moore, Abstr., 1894, i, 102); he has not, however, arrived at a definite result as to its nature. The coloration is produced when a solution containing only nickelous cyanide is subjected to similar treatment, but it is destroyed on shaking the solution with air. Both potassium nickelocyanide and solid nickelous cyanide, when warmed with alkaline hydroxylamine solution, give a red coloration which does not disappear on shaking; this coloration is not, however, produced in presence of excess of potassium cyanide; indeed, the addition of excess of that reagent decolorises the liquid. As Moore has observed, sodium amalgam readily reduces potassium nickelocyanide, the coloration which is produced rapidly vanishes, however, when the liquid is shaken. Alkali cyanide compounds of cobalt, platinum and zinc give no coloration with zinc dust, sodium amalgam, or hydroxylamine, but with alkaline solutions of hydroxylamine, alkali manganocyanides give a red coloration which is not destroyed by excess of potassium cyanide. When the red solution obtained by heating potassium nickelocyanide with alkaline hydroxylamine is shaken with pyridine, the colouring matter is taken up by the latter; if the pyridine solution is evaporated to a small volume, filtered from potassium chloride, and, after the lapse of some time, the unaltered potassium nickelocyanide is removed, it is found to have the property of reducing solutions of mercuric and silver salts, and to give a bright blue precipitate with hydrochloric acid. When the solution is evaporated to complete dryness, and again taken up with pyridine, a deep blue liquid is formed, from which, on the addition of water, an ultramarine-blue compound separates, which is insoluble in water, alcohol, ether, chloroform, &c., and becomes paler on keeping.

The author then enters into a theoretical discussion on the compounds of ammonia and organic bases with certain metallic salts, and he gives bibliographical references relating thereto. According to the constitutional formulæ proposed by Werner (*Zeit. anorg. Chem.*, **3**, 267) and by Jörgensen, stereoisomerides should exist of the compounds $RCl_2,2C_5NH_5$ (R = a metallic element), but the author has failed to observe them.

Dipyridine cobaltous chloride, $CoCl_2,2C_5NH_5$, is obtained when the calculated amount of pyridine is added to solid hydrated cobaltous chloride, and the mixture boiled with alcohol; it crystallises from alcohol in bluish needles, becomes darker at 120°, and melts at 192°. Its aqueous solution is red, and the chlorine is quantitatively precipitated therefrom on addition of silver nitrate; it gives the following

reactions:—With potassium cyanide, a greenish-yellow precipitate soluble in excess; with sodium platinic chloride (warmed), a yellow crystalline precipitate; with potassium ferrocyanide, an emerald-green precipitate; with potassium ferricyanide, a bluish-green precipitate. The compound loses pyridine and becomes red if exposed to the air, and when heated at 106° it becomes bright blue with the loss of pyridine (1 mol.).

Tetrapyridine cobaltous chloride, $CoCl_2,4C_5NH_5$, is obtained by treating anhydrous cobaltous chloride with more than six molecular proportions of pyridine, and subsequently boiling; the compound, after being recrystallised from pyridine, is peach-red; it becomes blue at 70°, partially melts at 124°, and fuses complete at 192—195° (the melting points of dipyridine cobaltous chloride).

Dipyridine nickelous chloride, $NiCl_2,2C_5NH_5$, crystallises from alcohol in yellowish, felted needles.

Diquinoline cobaltous chloride, $CoCl_2,2C_9NH_7$, is obtained when quinoline, in excess or otherwise, is added to hydrated cobaltous chloride; it separates from alcohol in blue crystals, commences to sinter at 150°, and melts at 192—200°. When boiled with water, a red solution is obtained which exhibits the following reactions:—With mercuric chloride or silver nitrate, white precipitates; with copper chloride, a greenish precipitate; with sodium platinic chloride, a yellow, crystalline precipitate; with hydrochloric acid, a yellow precipitate; with potassium dichromate, a yellow precipitate soluble in excess; with iodine and potassium iodide, a reddish-brown precipitate soluble in hydrochloric acid.

When anhydrous cobaltous chloride is heated with an excess of quinoline, a mixture of blue and red crystals separates on cooling; if these are boiled with a mixture of alcohol and quinoline, and subsequently with alcohol alone, a blue compound, *pentaquinoline dicobaltous chloride*, $2CoCl_2,5C_9NH_7 + H_2O$, remains; it melts at 178°. From the quinoline alcoholic extract, *tetraquinoline cobaltous chloride*, $CoCl_2,4C_9NH_7$, a red compound, separates; it is purified by washing with water. It becomes blue at 125°, and melts at 155—158°; if heated for several hours at 106°, it loses 2 mols. of quinoline, forming *diquinoline cobaltous chloride*, $CoCl_2,2C_9NH_7$, which melts at 192—195°.

A. R. L.

Ethane and Propane. A Correction. By K. Olszewski (*Ber.*, 1894, **27**, 3305—3306).—Referring to L. Meyer and Hainlen's recent papers on this subject (this vol., i, 1), the author states that five years ago he experimented with liquid ethane and propane (*Abhand. Krakau. Akad. Wiss*, 1889). Both substances were purified by repeated distillation at low temperatures. Ethane boils at −93° (1 atmos.); the critical temperature is 34°, under the critical pressure of 50·2 atmos. Propane boils at −45° (1 atmos.); the critical temperature is 97°, under the critical pressure of 44 atmos. Both compounds remain liquid at −151°. The vapour pressures at other temperatures are given, and seem to be in accord with those of Meyer and Hainlen at neighbouring temperatures.

J. B. T.

Carbon Tetriodide, Tetrabromide, and Tetrachloride. By Robineau and Rollin (*Chem. Centr.*, 1894, i, 1140—1141; from *Mon. Sci.*, **13**, 341—342).—Carbon tetriodide is obtained by heating a solution of potassium iodide (10 grams), 25 c.c. of soda of 36° B., and 100 c.c. of water at 80—90°, and then adding 1 c.c. of acetone and 50 c.c. of a 45 per cent. solution of sodium hypochlorite. The carbon tetriodide is obtained in red flocks; it crystallises from chloroform in red octahedra, is decomposed by fuming nitric acid, and reduced by sodium hyposulphite.

Carbon tetrabromide is obtained in white flocks on adding to a strongly alkaline solution of sodium hypobromite, heated at 70—80°, acetone in quantity insufficient to decolorise the mixture. If an excess of acetone is used, bromoform is obtained. The tetrabromide is also obtained on treating a hot solution of a hypochlorite with an alkaline solution of potassium bromide and a little acetone.

Carbon tetrachloride is formed by the action of sodium hypochlorite and soda heated at 60—70° on chloroform. A better result is obtained by employing 2,000 parts of sodium hypochlorite of 45 per cent., 200 parts of soda of 36° B., and 16 parts of acetone, and heating the mixture in a reflux apparatus for three hours. When too much acetone is employed, a mixture of chloroform and the tetrachloride is obtained. Carbon tetrachloride is characterised by its boiling point, vapour density, and smell, its indifference to soda when heated in a sealed tube, and its insolubility in a saturated aqueous solution of carbon tetrachloride. Carbon tetrachloride may be detected in chloroform as follows:—1 c.c. of the sample of chloroform is heated in a sealed tube at 100°, together with 10 c.c. of soda of 36° B. and 10 c.c. of water; if the sample contains tetrachloride, oily drops are formed on cooling the mixture. By this means 1 per cent. of tetrachloride is easily detected. Another method is to shake 1 c.c. of the sample of chloroform with 400 c.c. of a saturated aqueous solution of the tetrachloride, when, if tetrachloride is present in the sample of chloroform, a turbidity is produced. 0·1 per cent. of tetrachloride may be detected by the latter method. E. C. R.

Sodium and Potassium Nitromethane. By N. Zelinsky (*Ber.*, 1894, **27**, 3406—3407).—These salts explode very readily, and attention is drawn to the danger of drying them in the water oven at 100°. M. O. F.

Decomposition Products of Glucose. By Allein and F. Gaud (*J. Pharm.*, 1894, [5], **30**, 300—305).—In the estimation of glucose by Fehling solution, it is known that a part of the glucose present escapes estimation. Gaud finds that this loss may be expressed by the formula $y = -0{\cdot}00004801x + 0{\cdot}02876359x^2$, where x = the true titre of the sugar solution and y = the error. With a view to discover the source of this error, the authors have investigated the liquors resulting from a large number of estimations. Besides tartronic acid (which they consider as the main product of the action), the authors obtain lactic, dihydroxyphenylpropionic, melassic, and glucic acids and catechol. They, therefore, believe that the error of

the Fehling reaction is due to the decomposing action of the alkali on a part of the glucose before the latter has been able to exert its reducing action on the copper solution. They propose substituting an ammoniacal solution of copper sulphate for the Fehling solution (see this vol., ii, 92). L. T. T.

Influence of Certain Proteïds on Solutions of Glycogen. By H. Schwiening (*Pflüger's Archiv*, 1894, **58**, 222—228).—Sugar often forms in solutions of glycogen mixed with proteïd, and the hypothesis has been advanced that the proteïd is the source of the ferment. In the present research, various forms of proteïd were added to solutions of glycogen, but the results were most irregular, and do not settle the question, as sugar sometimes appeared in the sterilised, sometimes in the unsterilised, samples. W. D. H.

Fungus Cellulose. By E. Winterstein (*Zeit. physiol. Chem.*, 1894, **20**, 342; compare Abstr., 1894, ii, 425).—E. Gilson (*La Cellule*, **11**, 1894) has described a nitrogenous substance mycosine, $C_{14}H_{28}N_2O_{10}$, which he has separated from the cell membrane of fungi.

The present communication urges a claim for priority, the author being the first to point out the presence of nitrogen compounds mixed with the cellulose of fungi. From the results of his analyses, he doubts whether it is a single substance. W. D. H.

Nitrogenous Decomposition Product of Fungus Cellulose. A Correction. By E. Winterstein (*Ber.*, 1894, **27**, 3508—3509).—In his previous paper on this subject (this vol., i, 80), it was stated that *Boletus edulis*, *Agaricus campestris*, and *Morchella esculenta*, when fused with potassium hydroxide at 180°, yield nitrogenous fungus cellulose; the substance cannot, however, be unaltered cellulose, as it is soluble in highly dilute hydrochloric acid (compare Abstr., 1894, ii, 425). J. B. T.

Isonitramines. By W. Traube (*Ber.*, 1894, **27**, 3291—3293; compare Abstr., 1894, i, 400).—Sodiomethylenedi-isonitramine has been obtained by MacDonald and Masson (Trans., 1894, 944) by the action of nitric oxide on an alcoholic solution of sodium ethoxide, whilst the author has always prepared it by adding acetone to this mixture. The constitution of the isonitramine group is probably represented by the formula $O<\begin{matrix}NR\\|\\N\cdot OH\end{matrix}$ or RN:NOH (*sic*; ? RN:NO·OH), since methylenedi-isonitramine, when reduced by sodium amalgam, yields hydrazine and ammonia, whilst with acid reducing agents it is converted into methylamine. The formula proposed by MacDonald and Masson, $CH_2[N(NO)\cdot OH]_2$ is rendered improbable by the fact that the nitrosohydroxylamine derivatives described by Wohl (Abstr., 1894, i, 409) and Bamberger (Abstr., 1894, i, 412) have properties which differ entirely from those of the isonitramines. When the salts of methylenedi-isonitramine are heated with hydrochloric acid, nitrous oxide and nitrous acid are evolved, whilst formaldehyde and hydroxylamine are also formed, together with a little hydrocyanic acid. It is prob-

able that formoxime is first produced, and this is confirmed by the fact that when the di-isonitramine of benzylic cyanide is treated in the same way, the isonitroso-compound can be isolated. The isonitramines corresponding with diethyl ketone, dipropyl ketone, deoxybenzoïn, the substituted ethylic acetoacetates, ethylic malonate, and its substituted derivatives, phenylacetic acid, the nitroparaffins, and the 1 : 3-diketones have all been prepared and are being further examined. A. H.

Hydroxylamineacetic and α-Hydroxylaminepropionic acids. By A. WERNER and E. SONNENFELD (*Ber.*, 1894, **27**, 3350—3354).—Hydroxylamineacetic acid is a syrup, which dries to a gummy mass.

α-Hydroxylaminepropionic acid was prepared in the same way as hydroxylamineacetic acid (Abstr., 1893, i, 501), using ethylic α-bromopropionate instead of chloracetate. *α-Benzenylamidoximepropionic acid hydrochloride*, $NH_2 \cdot CPh{:}N \cdot O \cdot CHMe \cdot COOH, HCl + H_2O$, melts at 168°; the *acid* itself melts at 129°, and its *esoanhydride* at the same temperature. The acid, when diazotised in hydrochloric acid solution, yields *α-benzenylchloroximepropionic acid*,

$$CPhCl{:}N \cdot O \cdot CHMe \cdot COOH,$$

which melts at 102°. This, when treated with sodium ethoxide, yields *α-ethylbenzhydroximepropionic acid*, which forms a *hydrochloride* decomposing at 168°, and, when heated with strong hydrochloric acid, yields *α-hydroxylaminepropionic acid*, $NH_2 \cdot O \cdot CHMe \cdot COOH$, which was obtained as a soft, gummy mass. C. F. B.

Decomposition of Fatty Acids by Oxidation at Ordinary Temperatures in the absence of Ferments. By O. FRANK (*Chem. Centr.*, 1894, i, 1143; from *Arch. Physiol.*, 1894, 51—57).—The salts of the higher fatty acids, such as oleïc and stearic acids, are decomposed by the oxygen of the air at ordinary temperatures, especially when the oxidised acid, which is formed, is removed from the sphere of action. This decomposition is especially important in the case of ethereal extracts of animal tissues, such as occur in the separation of cholesterol from fat by Hoppe-Seyler's method, where the fat is hydrolysed and extracted with ether. This method gives results which are too high. By employing basic salts, the oxidation of the fatty acid can be considerably lessened. E. C. R.

Constitution of Ricinoleïc acid and its Derivatives. By P. WALDEN (*Ber.*, 1894, **27**, 3471—3478).—According to the formulæ proposed for ricinoleïc acid by Krafft,

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH{:}CH \cdot [CH_2]_8 \cdot COOH$$

(Abstr., 1888, 1270), and Goldsobel,

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH_2 \cdot CH{:}CH \cdot [CH_2]_7 \cdot COOH$$

(this vol., i, 81), this substance contains an asymmetric carbon atom as well as an ethylenic linking. The author has studied the application of the stereochemical theory to this compound and its deriva-

tives, and has also determined their behaviour towards polarised light. Three isomeric acids, $OH \cdot C_{17}H_{32} \cdot COOH$, are known. Ricinoleïc acid, melting at 16—17°, is optically active and dextrorotatory, $[\alpha]_D = 6{\cdot}25°$ to $7{\cdot}5°$. Ricinelaïdic acid, melting at 53°, is also dextrorotatory; in acetone solution at 20°, $[\alpha]_D = 4{\cdot}8°$ to $5{\cdot}4°$. Ricinic acid, melting at 81—82°, is optically inactive. A fourth isomeride was obtained on one occasion by heating barium ricinelaïdate in a vacuum. It melts at 75°, and is optically inactive.

Two isomeric fatty acids, $C_{17}H_{31} \cdot COOH$, have been obtained by heating the two optically active, unsaturated acids or their barium salts. That prepared from ricinoleïc acid melts at 44—45°, whilst the isomeride melts at 53—54°; both are optically inactive.

Two isomeric trihydroxy-acids are formed by the oxidation of ricinoleïc acid with potassium permanganate. One of these melts at 110—111°, and is levorotatory. In acetic acid solution, $[\alpha]_D = -6{\cdot}25°$ to $-6{\cdot}0°$. The other melts at 140—142°, and is probably optically active, although the author has not examined it. The corresponding acid, obtained from ricinelaïdic acid, melts at 114—115°, and is also probably optically active.

These facts are all consistent with the supposition that ricinoleïc acid is related to ricinelaïdic acid in the same way as maleïc to fumaric acid.

A number of other compounds were also examined with respect to their optical activity. Castor oil itself is dextrorotatory, α_D = about +3° for a length of 100 mm. Œnanthol, undecylenic acid, and caprylic acid, prepared from ricinoleïc acid, are optically inactive. The *phenylhydrazide* of *ricinoleïc acid*, melting at 62—63°, is dextrorotatory, $[\alpha]_D = +6{\cdot}6°$ in alcoholic solution. The corresponding derivative of ricinelaïdic acid melting at about 110° is also dextrorotatory, $[\alpha]_D = +7{\cdot}0°$ in alcoholic solution, whilst that of ricinic acid, which melts at 110—110·5°, is inactive. Ricinostearolic acid, $OH \cdot C_{17}H_{30} \cdot COOH$, prepared from ricinoleïc acid, is dextrorotatory, $[\alpha]_D = +13{\cdot}67°$ in solution in acetone. Sulphoricinic acid is inactive.

A. H.

Fusion of Stearolic and Behenolic acid with Potash. By M. Bodenstein (*Ber.*, 1894, **27**, 3397—3405).—Marasse (*Ber.*, **2**, 359) obtained hypogæic and myristic acids on fusing stearolic acid with caustic potash, 1 mol. of acetic acid being eliminated at each stage of the decomposition. The author has confirmed this observation, and determined the constitution of the former acid in the following manner (compare J. Baruch, Abstr., 1894, i, 170).

Palmitolic acid, $CH_3 \cdot [CH_2]_7 \cdot C{:}C \cdot [CH_2]_5 \cdot COOH$, is obtained from hypogæic acid by hydrolysis of the dibromide with alcoholic potash. When treated with concentrated sulphuric acid, it yields ketopalmitic acid, $CH_3 \cdot [CH_2]_7 \cdot CO \cdot [CH_2]_6 \cdot COOH$, which is converted by hydroxylamine into ketoximepalmitic acid, $C_8H_{17} \cdot C(NOH) \cdot [CH_2]_6 \cdot COOH$. Warm concentrated sulphuric acid effects molecular rearrangement of this substance, and the product, when heated with fuming hydrochloric acid at 180—200°, yields octylamine and pelargonic, amidoheptylic, and suberic acids. Hypogæic acid is, therefore, represented by the formula $CH_3 \cdot [CH_2]_7 \cdot CH{:}CH \cdot [CH_2]_5 \cdot COOH$.

Ketopalmitic acid melts at 74°. The *acid*, formed on warming ketoximepalmitic acid with concentrated sulphuric acid, crystallises from glacial acetic acid, and melts at 57·5—58°.

Icosenic acid, $C_{20}H_{38}O_2$, is formed when behenolic acid is heated with fused caustic potash at 250—270°; it melts at 50°, and boils at 267° under a pressure of 15 mm. The *sodium* and *barium* salts crystallise from alcohol; the *silver* salt is blackened by light, and the *lead* salt crystallises from ether. The *dibromide*, when hydrolysed with alcoholic potash, yields *icosinic acid*, $C_{20}H_{36}O_2$, which melts at 69°, and boils at 270° (15 mm.). Stearic acid is the sole product of the action of fused potash on behenolic acid when the temperature is maintained at 280—300°.

Attention is drawn to the points of analogy existing among members of the oleïc acid series. M. O. F.

Ethylic Formylsuccinate. By W. Wislicenus (*Ber.*, 1894, **27**, 3186—3189).—This substance is obtained by the action of dry sodium ethoxide suspended in ether on a mixture of ethylic succinate and formate; its *copper derivative* melts at 134—136°. Anderlini and Bovisi (Abstr., 1893, i, 193), for unknown reasons, assign the formula $COOEt{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt$ to this product. It should, of course, be $COOEt{\cdot}CH_2{\cdot}CH(CHO){\cdot}COOEt$; or, perhaps more probably, $COOEt{\cdot}CH_2{\cdot}C(:CH{\cdot}OH){\cdot}COOEt$, in which case it is the ethylic salt of the acid of which Fittig's aconic acid (Abstr., 1883, 458) is the lactone. It yields a sodium derivative, reacts with phenylhydrazine, can be reduced to ethylic itamalate (which boils at 110° under 15 mm. pressure), and is readily hydrolysed to alcohol and formic and succinic acids. C. F. B.

Condensation of Aldehydes with Glutaric acid. By R. Fittig (*Annalen*, 1894, **282**, 334—338).—General and introductory remarks on the papers of Roedel (this vol., i, 141) and Bronnert (next abstract). A. R. L.

Condensation of Isovaleraldehyde with Glutaric acid. By R. Fittig and E. Bronnert (*Annalen*, 1894, **282**, 344—362).—*Isovalerylideneglutaric acid*, $CHMe_2{\cdot}CH_2{\cdot}CH{:}C(COOH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed by heating a mixture of isovaleraldehyde, sodium glutarate, and acetic anhydride at 150°; it is also produced by the interaction of isovaleraldehyde with ethylic glutarate and sodium ethoxide (Claisen's reaction, Abstr., 1890, 891). The latter method is the more convenient, as the product is more easily purified; from ethylic glutarate (100 grams), isovaleralglutaric acid (3 grams), and diisovaleralglutaric acid (10 grams) are obtained. If metallic sodium is used instead of sodium ethoxide, there are obtained from ethylic glutarate (28 grams), isovalerylideneglutaric acid (1 gram), and diisovalerylideneglutaric acid (4 grams). Isovalerylideneglutaric acid crystallises from water in small plates, and melts at 75°; sodium amalgam is without action on the acid, but reduction appears to take place with hydriodic acid and phosphorus at 170°. The *barium* and *calcium* salts crystallise with 1 mol. H_2O, and are less soluble in hot than cold

water; the *silver* salt is a white precipitate, stable towards light and insoluble in water.

Dibromisoamyloglutaric acid,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CBr(COOH)\cdot CH_2\cdot CH_2\cdot COOH,$$

is prepared by treating a solution of isovalerylideneglutaric acid in carbon bisulphide with bromine in diffused sunlight; it melts at 148°.

Bromisoamyloglutaric acid,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CH(COOH)\cdot CH_2\cdot CH_2\cdot COOH,$$

is prepared by treating isovalerylideneglutaric acid with a saturated solution of hydrogen bromide in glacial acetic acid at 0°; it melts at 109°. The constitution of the acid is proved by the fact that when boiled with water for eight hours it yields an acid isomeric with the above-described isovalerylideneglutaric acid; this melts at 117·5°, and is probably the *lactonic acid*, $CHMe_2\cdot CH_2\cdot CH<\begin{matrix}CH(COOH)\\O—CO\cdot CH_2\end{matrix}>CH_2$. The chief product of the interaction of the brominated acid with water is, however, *isononenic acid* (*isovalerylidenebutyric acid*), $CHMe_2\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot COOH$, which is a colourless liquid volatile with steam. The *calcium* salt crystallises with $9H_2O$, and the *barium* salt with $1\frac{1}{2}H_2O$, whilst the *silver* salt is a white, amorphous precipitate which becomes brown when heated with water. *Dibromisononylic acid*, $C_9H_{16}Br_2O_2$, obtained by brominating isononenic acid in diffused sunlight, forms asymmetric crystals, $a : b : c = 0{\cdot}6829 : 1 : 0{\cdot}32876$, and melts at 66°. When isovalerylideneglutaric acid is distilled, an oil, consisting of the *anhydride*, $C_{10}H_{14}O_3$, passes over at 320°.

Diisovalerylideneglutaric acid, $CH_2[C(COOH){:}CH\cdot CH_2Pr^{\beta}]_2$ (mentioned above), can be prepared from its calcium salt, which is almost insoluble in water; it crystallises from acetone in lustrous, monosymmetric tablets, $a : b : c = 4{\cdot}8644 : 1 : 2{\cdot}2147$, melts at 220°, commences to decompose at 240°, and is as good as insoluble in cold water. The *silver* salt is a white precipitate soluble in hot water, and in the dry state is stable towards light. *Diisovalerylideneglutaric acid* forms a *dibromide*, $C_{15}H_{24}Br_2O_4$, which melts and decomposes at 185—186°, and yields the original non-brominated acid when treated with sodium amalgam; it also forms a *tetrabromide*, $C_{15}H_{24}Br_4O_4$, melting at 172°, and a *dihydrobromide*, $C_{15}H_{26}Br_2O_4$, melting at 174°, and decomposing at 180°. A. R. L.

Aconic acid. By H. Reitter (*Ber.*, 1894, **27**, 3440—3441).—Methylic aconate is best prepared by simply dissolving the acid in methylic alcohol at a gentle heat and allowing the solution to remain. It reacts with phenylhydrazine to form a compound, $C_{18}H_{20}N_4O_3$, which crystallises in white needles and melts at 167°. It is possibly a hydrazone-hydrazide of methylic formylsuccinate (compare Wislicenus, this vol., i, 127). Aconic acid also reacts with phenylhydrazine, forming a substance which is probably the hydrazone-dihydrazide of methylic formylsuccinate. It crystallises in colourless needles and melts at 178—179°. A. H.

Ethylic Allylenetetracarboxylate. By N. ZELINSKY and A. DOROSCHEWSKY (*Ber.*, 1894, **27**, 3374—3376).—When an alcoholic solution of ethylic disodiomalonate is boiled with carbon tetrachloride, a reaction takes place with separation of sodium chloride. After distilling off the alcohol and unaltered carbon tetrachloride, water is carefully added, the product of the reaction then separating as a yellow, granular crystalline mass, which is purified by recrystallisation from alcohol. The authors expected that this would prove to be *ethylic allylenetetracarboxylate*, $C(COOEt)_2{:}C{:}C(COOEt)_2$, but it was found that the substance still contains considerable quantities of sodium; on analysis it was found to have the composition $C_{17}H_{25}O_9Na$, and is, therefore, an additive compound of ethylic allylenetetracarboxylate and sodium ethoxide, the constitution of which is probably represented by the formula $CNa(COOEt)_2{\cdot}C(OEt)(COOEt)_2$. On treatment with sulphuric acid, it is converted into the corresponding *ethylic ethoxypropylenetetracarboxylate*,

$$C(COOEt)_2{:}CH{\cdot}C(OEt)(COOEt)_2,$$

which separates as a colourless oil; on attempting to distil it under 30 mm. pressure, alcohol was evolved at a low temperature, and the residual product then passed over at about 200°, solidifying in the receiver to a crystalline mass. The latter, after recrystallisation from boiling ether, forms acicular crystals melting at 93—95°, which, from the method of preparation, must in all probability consist of ethylic allylenetetracarboxylate, a supposition which is confirmed by the analysis. When allowed to remain in a moist atmosphere, it deliquesces, forming a colourless, syrupy liquid having the composition $C_{15}H_{20}O_8 + 2H_2O$. Further experiments with this substance are in progress, and attempts are being made to obtain free allylenedicarboxylic acid. H. G. C.

Uroxanic and Oxonic acids. By E. SUNDWIK (*Zeit. physiol. Chem.*, 1894, **20**, 335—341).—An alkaline solution of uric acid, when kept for some months in a closed vessel, deposits crystals of the uroxanate and oxonate of the alkali. These simple oxidation derivatives of uric acid (uroxanic acid, $C_4H_5N_3O_4$, and oxonic acid, $C_5H_8N_4O_8$) can, however, be prepared more rapidly as follows. If potassium permanganate is added to uric acid suspended in water, allantoïn is formed; but if the permanganate is added very carefully and gradually in the cold to an alkaline solution, uroxanic acid is obtained, which crystallises out after the manganese dioxide has been filtered off. Its silver, sodium, potassium, barium, and calcium salts were prepared.

Oxonic acid is prepared from the mother liquor from which the uroxanate has crystallised, by boiling, filtering, and then adding acetic acid in the cold. W. D. H.

Nature of the Aluminium Chloride Reaction. By C. RADZIEWANOWSKI (*Ber.*, 1894, **27**, 3235—3238).—In the synthesis of aromatic hydrocarbons by the action of alkylic haloïds on benzene and analogous compounds, a large amount of the material is lost, owing to the formation of higher alkylated compounds. The yield of a

hydrocarbon, such as ethylbenzene, may be greatly increased by using a larger amount of the solvent, in this case benzene, and, still further, by treating the higher boiling products with benzene and aluminium chloride, when these are converted into ethylbenzene. The yield of diphenylmethane from benzylic chloride and benzene may be increased in a similar manner, although not to so great an extent; the best results are obtained by using a large excess of benzene and keeping the mixture at 7°. In addition to diphenylmethane, two hydrocarbons are formed, melting at 86° and 78° respectively, and identical with the α- and β-dibenzylbenzenes described by Zincke (this Journal, 1873, 631; 1876, i, 703) and Baeyer (this Journal, 1873, 884); the best yield of these hydrocarbons is obtained by the action of 30 grams of benzylic chloride on 150 grams of diphenylmethane in presence of 7 grams of aluminium chloride.

When benzylic chloride (2 mols.) and benzene (1 mol.) are treated with aluminium chloride in carbon bisulphide solution, the chief product is the insoluble substance obtained by Perkin and Hodgkinson (Trans., 1880, 726), by the direct treatment of benzylic chloride with aluminium chloride. Friedel and Crafts regard this substance as a polymeric diphenylene, $(C_6H_4{:}CH_2)_x$, and this is in agreement with the fact that it is converted, by an excess of benzene and aluminium chloride, into diphenylmethane.

When diphenylmethane and asymmetrical diphenylethane are acted on by aluminium chloride in absence of benzene, they yield anthracene and mesodihydrodimethylanthracene respectively; as these hydrocarbons are also formed by the action of aluminium chloride on benzylic chloride and α-chlorethylbenzene respectively, it is evident that, in the above synthesis, the first action is the elimination of a phenyl group with formation of the chloride of the aromatic hydrocarbon residue, which then undergoes condensation into the corresponding anthracene hydrocarbon with elimination of hydrogen chloride. H. G. C.

Derivatives of Isodurene. By P. Jannasch and M. Weiler (*Ber.*, 1894, **27**, 3441—3448).—Isodurene is converted by bromine water into the dibromo-compound melting at 199°, no other derivative being formed. *Dinitroisodurene*, melting at 181°, is formed by the direct nitration of the hydrocarbon, and is accompanied by a smaller amount of dinitroxylene, melting at 112°. A dinitroisodurene, melting at 156° or 165°, could not be obtained (compare Jacobson, Abstr., 1883, 52; Ador and Rilliet, Abstr., 1879, 527). When the hydrocarbon is heated with dilute nitric acid at 115—130°, three monobasic acids are produced. These are isodurylic acid

$$[COOH : Me_3 = 1 : 3 : 4 : 5],$$

mesitylenecarboxylic acid $[COOH : Me_3 = 1 : 2 : 4 : 6]$, and β-isodurylic acid $[COOH : Me_3 = 1 : 2 : 3 : 5]$. The last-named acid has not been previously obtained pure; it crystallises in needles, and yields a *calcium* salt, which crystallises well. The acid may readily be separated from mesitylenecarboxylic acid by etherification, as the latter is not altered by treatment with alcohol and hydrogen chloride. A. H.

Diphenylic Thiocarbonate. By H. Eckenroth and K. Kock (*Ber.*, 1894, **27**, 3410—3412; compare Abstr., 1894, i, 408).—It is found that nitric acid converts diphenylic thiocarbonate into diphenylic carbonate, and the following homologues have been prepared, in order to ascertain whether the corresponding carbonates are formed under similar conditions. In each case, thiocarbonic chloride was allowed to act on the sodium derivative of the phenol.

Paradicresylic thiocarbonate, $CS(O\cdot C_7H_7)_2$, crystallises from alcohol in white needles, which melt at 132°. *Dithymylic thiocarbonate*, $CS(O\cdot C_{10}H_{13})_2$, forms white plates, and melts at 110°. *β-Dinaphthylic thiocarbonate*, $CS(O\cdot C_{10}H_7)_2$, crystallises from benzene in snowy plates, which melt at 212°; the *dibromo*-derivative, $C_{21}H_{12}Br_2O_2S$, crystallises from glacial acetic acid in minute plates, which melt at 171°. β-Dinaphthylic thiocarbonate is analogous to diphenylic thiocarbonate in its behaviour towards ammonia and amines (*loc. cit.*). M. O. F.

Action of Chlorine on Catechol and Amidophenol. By T. Zincke (*Ber.*, 1894, **27**, 3364—3366).—In a previous paper (Abstr., 1893, i, 698), the author and Küster showed that a number of different acids of the composition $C_4Cl_5\cdot COOH$, obtained from the hexachloroketopentenes, all yield the same acid, $C_4H_7\cdot COOH$, on reduction, and they regarded the latter as ethylidenepropionic acid. They were, however, unable to convert this acid into valerolactone in the manner described by Fittig, and suggested that Fittig's preparation may have contained allylacetic acid. Further investigation has shown that this supposition is incorrect, and that, under the exact conditions given by Fittig in a later paper, the acid in question may be readily converted into valerolactone; with bromine, moreover, it yields the same dibromide as Fittig's acid, so that there can now be no doubt as to the complete identity of the two compounds.

H. G. C.

Mercuric Picrate. By R. Varet (*Compt. rend.*, **119**, 559—561).—Mercuric picrate is obtained in brilliant, orange needles, of the composition $Hg[O\cdot C_6H_2(NO_2)_3]_2 + 4H_2O$, by adding freshly-precipitated and undried mercuric oxide, in successive small quantities, to a solution of picric acid kept at 80°. At first, it dissolves somewhat rapidly, but prolonged boiling is necessary in order to obtain complete saturation. The picrate is somewhat soluble in water, and, unlike the acetate, is not converted into a basic salt when the aqueous solution is boiled. When heated at 130°, it becomes completely dehydrated, and decomposes slightly with volatilisation of picric acid.

The action of acids on mercuric picrate, and of other mercuric salts on picric acid and alkali picrates, yield the following numbers.

Heat of dissolution of anhydrous mercuric picrate ..	− 4·7 Cal.
„ „ hydrated „ „ ..	−12·4 „
Heat of hydration of mercuric picrate (liquid H_2O)	+ 7·7 „
HgO ppt. + $2C_6H_2(NO_2)_3\cdot OH$ diss. = $Hg[C_6H_2(NO_2)_3O]_2$ diss. + H_2O, liquid develops	+ 6·2 „

HgO ppt. + $2C_6H_2(NO_2)_3\cdot OH$ solid = $Hg[C_6H_2(NO_2)_3O]_2$ sol. + H_2O sol. ...	develops	− 4·0 Cal.
$2[C_6$ (diamond) + H_2 gas + N_3 gas + O_6 gas + O gas] + Hg liquid = $Hg[C_6H_2(NO_2)_3O]_2$ solid.....	„	+44·35 „

In the value of the heat of neutralisation, mercuric picrate resembles the acetate. It is noteworthy that, whereas picric acid will completely displace hydrocyanic acid from dissolved potassium cyanide, with development of +10·7 Cal., hydrocyanic acid completely displaces picric acid from dissolved mercuric picrate, with development of +12·2 Cal. C. H. B.

Action of Picric Acid and Picrates on Metallic Cyanides. By R. Varet (*Compt. rend.*, **119**, 562).—Isopurpurates are not formed by the action of mercuric cyanide on picric acid or picrates, and the author has shown (preceding abstract) that hydrocyanic acid completely displaces picric acid from mercuric picrate. This result affords further proof of the author's general conclusion (Abstr., 1891, 681) that, in the action of picric acid and picrates on metallic cyanides, isopurpurates are always formed if the picric acid displaces hydrocyanic acid from the particular cyanide, but are not formed if hydrocyanic acid displaces the picric acid, the inverse displacements being determined by the thermochemical disturbances. C. H. B.

The Bleaching Powder Reaction for Aniline. By R. Nietzki (*Ber.*, 1894, **27**, 3263—3264).—The well known bleaching powder reaction for aniline can be readily obtained by adding an excess of the reagent to a solution of aniline in water, and is given in equal intensity by commercial aniline and by aniline prepared with the greatest care from pure materials. The reaction must, therefore, be considered as due to the aniline itself and not to any impurity. (Compare Hantzsch and Freese, Abstr., 1894, i, 572; this vol., i, 24). A. H.

Thioaniline. By R. Nietzki and H. Bothof (*Ber.*, 1894, **27**, 3261—3263).—*Paradinitrophenylic sulphide* is formed when paranitrochlorobenzene, in alcoholic solution, is heated with sodium sulphide; it crystallises in yellow plates, melting at 154°. When reduced with zinc dust and acetic acid, it is converted into the thioaniline described by Merz and Weith; this result does not agree with that arrived at by K. A. Hofmann (this vol., i, 87), who looks on this substance as an ortho-compound. A. H.

New Modes of Formation of Thiodiphenylamine. By K. A. Hofmann (*Ber.*, 1894, **27**, 3320—3324; compare this vol., i, 87).—When aniline is heated with sulphur and hydrochloric acid at 170—200°, it seems that paradiamidophenylic bisulphide,

$$NH_2\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot NH_2,$$

is first formed, and that this then condenses with aniline to form

monophenyldiamidophenylic bisulphide, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$, which then breaks up partly into thiodiphenylamine,

$$C_6H_4<\begin{matrix}NH\\S\end{matrix}>C_6H_4,$$

and paramidothiophenol, $SH{\cdot}C_6H_4{\cdot}NH_2$. The actual products of the action are thiodiphenylamine and *phenyldiamidophenylic bisulphide*. The latter crystallises in yellow needles, and oxidises readily in the air; when reduced with tin and hydrochloric acid, it decomposes into paramidothiophenol and a basic compound, ($? C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}SH$), the hydrochloride of which forms a white, crystalline, readily oxidisable powder.

It will be noticed that in the above formation of thiodiphenylamine a migration of the sulphur atom has taken place from the para- to the ortho- position; other examples of this are cited.

C. F. B.

Benzylorthamidobenzylaniline. By M. Busch and H. Roegglen (*Ber.*, 1894, **27**, 3239—3247).—Hitherto only those derivatives of orthamidobenzylaniline have been prepared, in which substitution has taken place in the aliphatic amido-group. The authors endeavoured to obtain bisubstitution products by the action of alkylic haloids on the monosubstituted derivatives, but without success. The unsymmetrical dibenzyl-derivative may, however, be prepared indirectly by acting on orthamidobenzylaniline with benzaldehyde, and reducing the resulting benzylidineorthamidobenzylaniline,

$$CHPh{:}N{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh,$$

with sodium in alcoholic solution. The latter compound crystallises in spear-shaped needles melting at 107—108°, and is resolved by dilute sulphuric acid into its constituents. The product of reduction, *benzylorthamidobenzylaniline*, $CH_2Ph{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, crystallises from alcohol in spherical aggregates of lustrous, colourless plates, melting at 88°; it is a weak di-acid base, the *dihydrochloride*, $C_{20}H_{20}N_2,2HCl$, crystallising in colourless needles which decompose and melt at about 170°, and are dissociated by water. With acetic anhydride, both hydrogen atoms of the imido-groups are displaced by acetyl groups with formation of *diacetylbenzylorthamidobenzylaniline*, $CH_2Ph{\cdot}NAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPhAc$, which crystallises in slender, colourless needles melting at 173°; it behaves, therefore, towards this reagent in a manner different from the corresponding symmetrically substituted orthodiamine, which only takes up one acetyl group with formation of a ring derivative.

Nitrous acid acts on benzylorthamidobenzylaniline with formation of the *dinitroso*-derivative, $C_{20}H_{18}N_2(NO)_2$, which crystallises in fascicular aggregates of colourless plates melting at 124°; on reduction with zinc dust and acetic acid, it yields the monhydrazine derivative, the second nitroso-group being eliminated as ammonia. The *hydrazine* derivative, $C_{20}H_{21}N_3$, crystallises in tufts of white needles melting at 110°, and with benzaldehyde yields a *hydrazone*, crystallising in pale yellow needles melting at 140—142°.

When benzylorthamidobenzylaniline is heated on the water bath with benzaldehyde, it is converted into *benzyldiphenyltetrahydroquinazoline*, $C_6H_4<\begin{matrix}N(C_7H_7)\cdot CHPh\\ CH_2\text{——}NPh\end{matrix}$, which crystallises in colourless needles melting at 120°; the tetrahydroquinazoline ring is opened very readily, dilute sulphuric acid converting the above compound into its constituents on gentle heating. The corresponding 1′ : 2′ : 3′-*benzylhydroxyphenyltetrahydroquinazoline* is prepared in a similar way from salicylaldehyde and the diamine, and forms clear, colourless prisms melting at 172°. Carbon bisulphide does not act on the diamine at all readily, but at 180° an action takes place; the compound formed, however, is the same as the phenylthiotetrahydroquinazoline obtained from orthamidobenzylaniline, one of the benzyl groups being eliminated in the reaction. The *benzylphenylthiotetrahydroquinazoline*,

$$C_6H_4<\begin{matrix}N(C_7H_7)\cdot CS\\ CH_2\text{——}NPh'\end{matrix}$$

may, however, be obtained by heating the former compound with benzylic chloride, and crystallises in colourless needles melting at 93°. The entrance of the benzyl group into the molecule gives to the compound basic properties; the *nitrate*, $C_{21}H_{18}N_2S,HNO_3$, crystallises in large, transparent needles melting at 126° with evolution of gas.

Carbonyl chloride acts on benzylorthamidobenzylaniline, but does not form a ring derivative, the substance obtained having probably the constitution $CH_2Ph\cdot N(COCl)\cdot C_6H_4\cdot CH_2\cdot NPh\cdot COCl$; it crystallises in transparent prisms melting at 113°.

The following compounds have also been obtained by the action of salicylaldehyde and orthonitrobenzaldehyde on orthamidobenzylaniline; *orthohydroxybenzylidineorthamidobenzylaniline*,

$$OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CH_2\cdot NHPh,$$

crystallising in yellow needles and melting at 124°, and *orthonitrobenzylidineorthamidobenzylaniline*, $NO_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CH_2\cdot NHPh$, crystallising in yellow plates and melting at 132—134°.

H. G. C.

Paranitrodiazobenzene Methyl Ether. By E. Bamberger (*Ber.*, 1894, **27**, 3412—3420).—A detailed criticism of the arguments put forward by Hantzsch (this vol., i, 26) supporting his view that the ether is an "anti-" derivative. The author still regards it as a normal diazo-compound, and although this cannot be directly shown by hydrolysis, the hydrolytic conversion of diazobenzene methyl ether and parabromodiazobenzene methyl ether into the corresponding normal diazo-salts lends support to the view. M. O. F.

Action of Phthalic Chloride on Dinitrodiazoamidobenzenes. By B. Pawlewski (*Ber.*, 1894, **27**, 3430—3431).—*Paranitrophthalanil*, $C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_6H_4\cdot NO_2$, is formed when paradinitrodiazoamidobenzene is heated with phthalic chloride. It is a colourless, insoluble powder, which melts at 262—264°.

Metanitrophthalanil is obtained in a similar manner from metadinitrodiazoamidobenzene; the same product is formed on fusing a mixture of metanitraniline and phthalic anhydride (Gabriel, *Ber.*, **11**, 2260). It crystallises from boiling glacial acetic acid in long needles which melt at 242—244°.

The action of phthalic chloride on nitranilines gives rise to nitrophthalanil-derivatives. M. O. F.

Alkylated Azo-compounds, and the Theory of Dyeing. By R. Meyer and J. Schäfer (*Ber.*, 1894, **27**, 3355—3361).—In the dyeing of fabrics of animal origin, it is generally supposed that a union takes place between the fabric and the colouring matter, as only colouring-matters containing a salt-forming group, such as the hydroxy- or amido-group, are capable of direct dyeing. In the case of vegetable fabrics, which consist almost entirely of cellulose, it is difficult to suppose that any such combination takes place, as the cellulose shows so little tendency to enter into chemical combination; at the same time, it is remarkable that, as a rule, only those colouring matters containing salt-forming groups do dye vegetable fabrics directly. Certain cases are, however, known in which compounds supposed to contain no such group dye cotton directly, and the authors have examined some of these cases more closely.

The first colouring matter examined was that known as chrysophenin, which is obtained by the ethylation of "Brilliantgelb," and is usually supposed to have the constitution

$$C_2H_2[C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot OEt]_2.$$

The analysis of its salts has, however, shown that instead of two ethoxyl groups it contains one ethoxyl group and one hydroxyl group, and this is confirmed by the fact that, on treatment with zinc dust and acetic acid, it yields both paramidophenetoïl and paramidophenol. Another colouring matter which is supposed to contain no salt-forming group, although it dyes cotton directly, is obtained from diamidonaphthalenedisulphonic acid, and to it is assigned the constitution $C_{10}H_4(SO_3Na)_2(N_2\cdot C_6H_4\cdot OEt)_2$; further investigation, however, has shown that in this case also only one of the hydroxyl groups is ethylated.

Attempts were then made by the authors to obtain the dibenzyl derivative of "Brilliantgelb," $C_2H_2[C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot O\cdot C_7H_7]_2$, but it was found impossible to displace the hydrogen atoms of both hydroxyl groups, only the monobenzyl derivative being obtained. An endeavour was next made to obtain the dialkyl derivative of a bisazo-compound containing no sulphonic groups, diphenylbisazophenol being selected, and subjected to the action of benzylic chloride and soda. Here again, however, the action stopped with the formation of the monobenzyl derivative. In all the cases examined, therefore, the alkyl derivatives of symmetrical hydroxyazo-compounds have proved to be unsymmetrical mono-ethers. H. G. C.

Action of Alkalis on Orthonitrophenylhydrazine. By R. Nietzki and E. Braunschweig (*Ber.*, 1894, **27**, 3381—3384).—The preparation of azoimide by the action of alkalis on dinitrobenzene-

diazoimide led one of the authors to try whether it was not possible to obtain hydrazine in a similar manner by the action of alkalis on orthonitrophenylhydrazinesulphonic acid; it was found, however, that hydrazine is not formed in this manner, but, on the addition of acids, a colourless, crystalline compound separated. As this appeared to belong to a new class of compounds, the authors have studied the action more closely, using, however, the simpler orthonitrophenylhydrazine. The latter is very readily acted on by warm alkalis, even by aqueous ammonia, and, on the addition of acids, the product of the reaction separates in colourless needles melting at 157°, and having the composition $C_6H_5N_3O$; it is therefore formed from orthonitrophenylhydrazine by the removal of the elements of water. It is a fairly strong acid, and yields sparingly soluble salts with the alkaline earth and heavy metals, the *lead* salt forming colourless plates, which explode at 270°. It is a very stable substance, and is not acted on by acetic anhydride or reducing agents, and therefore no longer contains a nitro-group. When the lead salt is heated with ethylic iodide at 180°, iodine is separated and lead iodide formed, and the solution yields dark crystals, which have a metallic lustre, and resemble the periodides of the ammonium bases. To remove the iodine, it was treated with silver chloride, and the resulting chloride, which does not crystallise, converted into the *platinochloride* $(C_{10}H_{13}N_3)_2,H_2PtCl_6$; the new base is therefore formed by the displacement of one atom of oxygen by two ethyl groups. The same derivatives may also be obtained from azimidobenzene by heating it with ethylic iodide and sodium ethoxide at 150°; the product of the action, when treated with iodine, yields the periodide above described, and this, on treatment with silver chloride and chloroplatinic acid, is converted into a platinochloride identical with that already mentioned. The original substance must therefore be closely allied to azimidobenzene, and, taking into consideration its properties and mode of formation, the authors believe that it has undoubtedly the constitution $C_6H_4<\overset{N(OH)}{\underset{\quad N}{\quad}}>N$, and propose to term this class of compound *azimidoles*. The compound obtained by the action of ethylic iodide on both azimidole and azimidobenzene must then have the constitution $C_6H_4<\overset{NEt_2I}{\underset{\quad N}{\quad}}>N$.

The substance obtained by the action of alkalis on orthonitrohydrazinesulphonic acid is the corresponding *azimidolesulphonic acid*; its *disodium* salt, $C_6H_3N_3Na_2SO_4 + H_2O$, separates in colourless needles, which are converted by the action of dilute acids into the *monosodium salt* $C_6H_4N_3SO_4Na + H_2O$, a sparingly soluble substance, crystallising in needles. The free acid has not yet been prepared.

H. G. C.

Action of Hydrazine on Imidoethers. By A. Pinner and N. Caro (*Ber.*, 1894, **27**, 3273—3291; compare Abstr., 1893, i, 710; 1894, i, 385).—Paratolenylimidoethyl ether reacts in a similar manner to the benzimido-compound. *Paratolenylhydrazidine*,

$$NH_2\cdot NH\cdot C(NH)\cdot C_7H_7,$$

forms long prisms, which melt and decompose at 75—77°. It is strongly basic, absorbing carbonic anhydride from the air, and has powerful reducing properties. The *carbonate* crystallises in prisms, and melts and decomposes at 100°; the *picrate* melts at 162°, and the *nitrate* at 106° with violent decomposition. In acid solution, it reacts with benzaldehyde to form *benzylidenetolenylhydrazidine*, which crystallises in white plates, and melts at 154°, whilst in alkaline solution, benzaldehyde yields *tolenylhydrazine benzoate*, melting at 244°. *Glyoxaleneditolenylhydrazidine*, $C_2H_2[N{\cdot}NH{\cdot}C(NH){\cdot}C_7H_7]_2$, forms yellow plates, and melts at 252°. *Paratolyltetrazotic acid*, $C_7H_7{\cdot}C\begin{matrix}N{-}N\\ \|\\ NH{\cdot}N\end{matrix}$, is obtained by the action of nitrous acid on the hydrazidine; it forms flat prisms, and melts at 234°, becoming red and frothing up at the same time. It is a strong acid, and decomposes carbonates; the *silver* salt is a white, crystalline powder. Acetic anhydride does not yield an acetyl derivative but a mixture of acetyltolylamidine and ditolylmethylcyanidine. It is remarkable that diazobenzene chloride does not give the expected diazo-compound with tolenylhydrazidine, but converts it into tetrazotic acid.

Benzoyltolenylhydrazidine crystallises in colourless plates, and melts at 170°. It is soluble both in acids and in alkalis, and acts as a strong reducing agent. When it is heated at 120°, it is converted into the non-reducing *phenyltolyltriazole*, $C_7H_7{\cdot}C\begin{matrix}N{-}CPh\\ \|\\ NH{\cdot}N\end{matrix}$, which crystallises in white plates melting at 170°. *Toluoyltolenylhydrazidine* resembles the benzoyl compound, and, when heated, passes into ditolyltriazole, which is described below.

Ditolenylhydrazidine, $N_2[C(C_7H_7){\cdot}NH_2]_2$, forms pale yellow plates, and is sparingly soluble in hot alcohol and acetone. Although stable towards alkalis, it is readily converted by acids into ditolyltriazole, and the same change occurs when it is heated. At 196°, the hydrazidine melts, solidifies again slightly above this temperature, and then finally melts at 248°, the melting point of the triazole. The *hydrochloride* crystallises in stellate groups of needles, the *platinochloride* decomposes above 300°, the *aurochloride* melts at 154—155°, and the *nitrate* at 123°. The *diacetyl* derivative forms long, white needles melting at 185°.

The reaction of ditolenylhydrazidine with nitrous acid is similar to that of dibenzenylhydrazidine. With 2 mols. of sodium nitrite and dilute acetic acid, it yields tolyltetrazotic acid and toluonitrile. With 1 mol. of the nitrite and dilute hydrochloric acid, it forms the hydrochloride of toluoyltolenylhydrazidine, identical with that obtained by the action of toluic chloride on tolenylhydrazidine, whilst with 4 mols. of nitrite and dilute hydrochloric acid, it is converted into the *hydrochloride* of *toluoylnitrosotolenylhydrazidine*, $C_7H_7{\cdot}C(N{\cdot}NO){\cdot}NH{\cdot}NH{\cdot}CO{\cdot}C_7H_7,HCl + \frac{1}{2}H_2O$. This substance forms colourless prisms, melts and deflagrates at 119°, and, when boiled with water, yields nitrous acid and toluoyltolenylhydrazidine. The free base could not be prepared from the hydrochloride.

Toluoyltolenylhydrazidine, the formation of which has been described above, crystallises in short, compact prisms, and is soluble in

strong alkalis and dilute acids. Its *hydrochloride* melts at 203°. Both this salt and the free base reduce copper salts on boiling. When heated, the base is converted into *ditolyltriazole*,

$$C_7H_7\cdot C\begin{<}N\text{—}C\cdot C_7H_7\\ NH\cdot N\end{>},$$

which crystallises from alcohol in colourless prisms, melts at 248°, and sublimes at a higher temperature. It does not reduce copper salts, and is insoluble in dilute acids. The *silver* salt decomposes at 240°. *Acetylditolyltriazole* forms prisms melting at 129—130°.

Ditolyldihydrotetrazine, $C_7H_7\cdot C\begin{<}N\text{——}N\\ NH\cdot NH\end{>}C\cdot C_7H_7$, crystallises in long, thin, yellow needles, which melt and become red at 235°, ditolyltetrazine (see below) being formed; in the moist state, it oxidises on exposure to air with formation of ditolyltetrazine, $C_{16}H_{14}N_4$, and is converted into this substance by other oxidising agents. When boiled with zinc dust and acetic acid, it is reduced, yielding a substance which has the composition of ditolyltriazole; it has not yet been found possible, however, to decide whether it is actually identical or only isomeric with the ditolyltriazole described above. When ditolyldihydrotetrazine is boiled with hydrochloric acid, it is partially converted into the isomeric ditolylisodihydrotetrazine, and partially decomposed with formation of ditolylbiazoxole and hydrazine. *Ditolylisodihydrotetrazine*, $C_7H_7\cdot C\begin{<}N\cdot NH\\ NH\cdot N\end{>}C\cdot C_7H_7$, crystallises in white prisms, melts without decomposing at 295°, and does not become red when treated with oxidising agents. The *aurochloride* melts at 183°. *Ditolylbiazoxole*, $C_7H_7\cdot C\begin{<}O\cdot C\cdot C_7H_7\\ N\cdot N\end{>}$, which is also formed by the action of sodium nitrite on a hydrochloric acid solution of toluoyltolenylhydrazidine, crystallises in lustrous, flat needles, is insoluble in acids and alkalis, and melts at 233—234°. It unites with 1 mol. of silver nitrate to form a double compound, $C_{16}H_{14}N_2O,AgNO_3$, which decomposes above 280°.

Ditolyltetrazine, $C_7H_7\cdot C\begin{<}N:N\\ N\cdot N\end{>}C\cdot C_7H_7$, crystallises in dark bluish-red, flat needles or plates, and melts at 233°. When boiled with alcoholic potash, it yields a compound of the formula, $C_{16}H_{16}N_2O$, the constitution of which has not been determined.

Under certain conditions of experiment, the action of hydrazine on tolenylimido-ether yields *ditolenylimidine*, $C_{16}H_{17}N_3$, which crystallises in long, compact needles, and melts at 161°. The *hydrochloride*, melting at 252°, and the *nitrate*, melting at 155°, are only sparingly soluble. The *aurochloride* melts and decomposes at 148°. *Triacetylditolylenylimidine* forms colourless needles, and melts at 117°.

A. H.

anti-Cinnamaldoxime. By E. Bamberger and C. Goldschmidt (*Ber.*, 1894, **27**, 3428—3430).—anti-*Cinnamaldoxime*,

$$C_6H_5\cdot CH{:}CH\cdot\underset{\|}{C}H$$
$$HO\cdot N$$

is formed, in addition to the syn-modification, when hydroxylamine hydrochloride is added to cinnamaldehyde suspended in caustic soda. Separation from the isomeride is effected by treatment with light petroleum (b. p. 40—70°); it melts at 64—65°. Hydrogen chloride converts it into the hydrochloride of the syn-oxime. The *acetyl* derivative, $C_9H_8{\cdot}NOAc$, melts at 35·5°, and during its preparation from the anti-modification the isomeric derivative is also formed; of these two derivatives, the latter only is hydrolysed by warm water.

M. O. F.

Preparation of Benzoic Anhydride. By L. Claisen (*Ber.*, 1894, **27**, 3182—3184).—Deninger (*J. pr. Chem.*, [2], **50**, 479) has found that benzoic chloride yields benzoic anhydride when treated with anhydrous sodium carbonate; the author has found that the latter, or, equally well, potassium carbonate, will often act as a condensation agent when hydrochloric acid has to be removed. For example, if aniline or phenol is dissolved in ether or benzene, powdered potassium carbonate added, and then benzoic chloride or ethylic chloroformate gradually added, condensation takes place. In a similar manner, it is often possible to replace one or both of the hydrogen atoms in the $\cdot CO{\cdot}CH_2{\cdot}CO\cdot$ group of 1 : 3-diketones by acid radicles. For example, ethylic acetoacetate yields a monobenzoic derivative; dibenzoylmethane and benzoylacetone both mono- and di-derivatives.

A convenient modification of the Schotten-Baumann method is also suggested. It is to use alcoholic sodium ethoxide (2 mols.) with 1 mol. of benzoic chloride and 1 mol. of the substance from which a benzoic derivative is to be prepared. The tedious process of shaking is thus avoided.

C. F. B.

A New Class of Cyclic Iodo-compounds from Iodophenylacetic acid. By W. Raum (*Ber.*, 1894, **27**, 3232—3235).—V. Meyer and his co-workers have shown that iodobenzoic acid can be readily converted into iodosobenzoic acid either by oxidation or by conversion into the iodochloride and acting on the latter with water. The iodosobenzoic acid thus formed exists in the two tautomeric forms $C_6H_4{<}^{IO}_{COOH}$ and $C_6H_4{<}^{I(OH)}_{CO}{>}O$, the latter containing a ring of five atoms. The author has carried out a similar series of reactions with iodophenylacetic acid, in order, if possible, to obtain compounds containing an analogous ring of six atoms.

Orthiodophenylacetic acid was obtained from orthiodotoluene, according to Mabery and Robinson's method, by acting on it with bromine, converting the orthiodobenzylic bromide thus formed into the corresponding nitrile, and subjecting the latter to hydrolysis. The pure acid melts at 110°, and not at 95—96° as stated by Mabery and Robinson. The corresponding *iodochloride*, $ICl_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}COOH$, is prepared by passing chlorine into a solution of the acid in chloroform, and forms yellow crystals, which on treatment with water do not yield the iodoso-derivative, but lose hydrogen chloride, forming the compound $C_6H_4{<}^{ICl\cdot O}_{CH_2{\cdot}CO}$.

From the composition alone, it might be supposed that the new substance was a mixture of the iodochloride with iodophenylacetic acid, but it behaves in all respects as a homogeneous compound, and is insoluble in ether, whereas both the above-named compounds are readily soluble in that liquid. The compound therefore takes an intermediate position between an iodoso-compound and an iodochloride, and contains the nucleus of six atoms whose formation was expected.

Similar experiments with pariodophenylacetic acid have led to totally different results, the iodochloride being reconverted by boiling water or alkalis into the original iodo-acid. H. G. C.

Ethylic Diazoacetate and Picric acid. By E. BUCHNER (*Ber.*, 1894, **27**, 3250—3251).—When ethylic diazoacetate is treated with picric acid and a little alcohol, nitrogen is evolved, and *ethylic trinitrophenylglycollate*, $C_6H_2(NO_2)_3 \cdot O \cdot CH_2 \cdot COOEt$, remains. It crystallises from alcohol in yellowish needles, and melts at 102°. It is not unlikely that other aliphatic diazo-compounds may react with picric acid in a similar manner, yielding crystalline substances, and this reaction might then be made use of for their recognition.

H. G. C.

Velocity of Coumarin Formation. By E. HJELT (*Ber.*, 1894, **27**, 3331—3333).—Coumaric, methylcoumaric, and isopropylcoumaric acids exhibit great velocity of coumarin formation, 40, 90, and 70 per cent. respectively undergoing conversion into the anhydride within 40 minutes, and this in spite of the fact that they are $\hat{c}$-hydroxy-acids. Probably the double bond conditions the existence of the cis-configuration, which is known to be favourable to anhydride formation. C. F. B.

Action of Benzylamine on Ethylic Acetoacetate. By R. MÖHLAU (*Ber.*, 1894, **27**, 3376—3380).—The action of ammonia, methylamine, and diethylamine on ethylic acetoacetate has been studied by numerous investigators, who have shown that the products are amido-derivatives of ethylic crotonate. According to the Le Bel-van't Hoff hypothesis, these substances should exist in two stereometric forms, but hitherto no such isomerides have been isolated. The author has therefore examined the action of an amine of higher molecular weight on ethylic acetoacetate, namely, benzylamine, and has succeeded in obtaining the two stereometric ethylic benzylamidocrotonates.

When benzylamine (1 mol.) is added to an ethereal solution of ethylic acetoacetate (1 mol.) at −5°, an additive product, probably of the constitution $CH_2Ph \cdot NH \cdot CMe(OH) \cdot CH_2 \cdot COOEt$, separates in slender needles, but after a time these disappear, and in their place compact crystals are deposited. This compound, which forms about half the product, crystallises in tasteless prisms melting at 79—80°, has the composition and molecular weight of an *ethylic benzylamidocrotonate*, $CH_2Ph \cdot NH \cdot CMe{:}CH \cdot COOEt$, and is distinguished as the α-derivative. When heated above its melting point, it is converted into the stereoisomeride, or β-derivative, which is also

contained in quantity in the original product of the action of benzylamine on ethylic acetoacetate, and is formed almost quantitatively if these two substances are not cooled well during the mixing. It crystallises in tabular prisms melting at 21—21·5°, is volatile in a current of steam, has a sweet, and at the same time peppery, taste, and, under the influence of light, is gradually transformed into the *a*-derivative.

Neither of the isomerides can be distilled, decomposition taking place at 270—300°; methane, hydrogen, and oxides of carbon pass off first, followed by ethylic acetate, acetone, and alcohol, whilst the residue contains dibenzylcarbamide and certain basic compounds.

When benzylamine and ethylic acetoacetate are heated together under pressure, the action proceeds in a different manner, a substance being formed which is either *benzyl-β-amidocrotonobenzylamide*, $CH_2Ph{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, or *benzyl-β-imidobutyrobenzylamide*, $CH_2Ph{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, as it is resolved by acids into benzylamine and *benzylacetoacetamide*,

$$COMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph,$$

which crystallises in prisms melting at 96—97°, and has no basic properties.

That the compounds above described have in reality the constitution assigned to them, and are not the isomeric ethylic benzyl-β-imidobutyrates, $CH_2Ph{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt$, is shown by the fact that benzylamine has no action on ethylic diethylacetoacetate, even at 100°. H. G. C.

Separation of the Dihydrophthalic Acids. By W. F. Proost (*Ber.*, 1894, **27**, 3185).—Dihydrophthalic acid, melting at 215° (Astié, *Annalen*, **258**, 188), was prepared, and its acid strychnine salt crystallised. The acid obtained from the crystals gave a sodium salt that was distinctly dextrorotatory; from the mother liquor a levorotatory sodium salt was obtained. C. F. B.

Condensation of Benzaldehyde with Glutaric acid. By R. Fittig and S. Roedel (*Annalen*, 1894, **282**, 338—344).—*Benzylideneglutaric acid*, $CHPh{:}C(COOH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is thus prepared. The product of the interaction of benzaldehyde, sodium glutarate, and acetic anhydride is submitted to distillation in a current of steam, whereby unaltered benzaldehyde is removed; the residue, after preliminary purification, is separated from benzoic and cinnamic acids by conversion into the calcium salts, the salt of the new acid being almost insoluble in hot water. The acid crystallises in silky needles, melts at 175°, and is almost insoluble in benzene, chloroform, and carbon bisulphide. The *calcium* and *barium* salts crystallise with $1H_2O$. The *silver* salt is a white, flocculent precipitate, stable towards light.

Benzylglutaric acid, $CH_2Ph{\cdot}CH(COOH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is obtained by reducing benzylideneglutaric acid with sodium amalgam. The *calcium* salt crystallises with $\frac{1}{2}$ mol. H_2O; the *barium* salt with

$2\frac{1}{2}$ mols. H_2O; and the *silver* salt is a white precipitate, stable towards light.

Dibromobenzylglutaric acid, $CHPhBr\cdot CBr(COOH)\cdot CH_2\cdot CH_2\cdot COOH$, is prepared by the action of bromine in diffused sunlight on benzylideneglutaric acid suspended in chloroform; it decomposes at 191—192° without melting.

Bromobenzylglutaric acid, $C_{12}H_{13}BrO_4$, is obtained by heating benzylideneglutaric acid with concentrated hydrobromic acid in a sealed tube at 100°; it melts and decomposes at 158—159°, and is practically insoluble in all ordinary indifferent solvents. A. R. L.

Synthesis of Unsaturated Dicarboxylic acids from Ketones and Diethylic Succinate. By H. Stobbe (*Annalen*, 1894, **282**, 280—319).—The synthesis of teraconic acid (γ-dimethylitaconic acid) by the action of sodium ethoxide on a mixture of acetone and diethylic succinate has already been described (Abstr., 1894, i, 15). The mixture of acids forming the secondary product probably contains the isomeric aticonic acid. Fittig (Abstr., 1893, i, 691) has named the acids which are formed by the action of alkalis on the itaconic acids, aticonic acids.

γ-Methylphenylitaconic acid, $COOH\cdot CH_2\cdot C(COOH):CMePh$, is prepared by the action of sodium ethoxide (2 mols.) on diethylic succinate (1 mol.) and acetophenone (2 mols.). The product is acidified, the crude crystalline mass dissolved in benzene, and carbon bisulphide added; the precipitated acid is then recrystallised from benzene or water. An isomeric aticonic acid is separated from the mother liquor (see below). γ-Methylphenylitaconic acid separates from water in lancet-shaped crystals, and melts and decomposes at 161—163°. The *barium* salt forms stellate groups of needles; the *silver* salt is a flocculent precipitate, tolerably stable towards light; and the *calcium* salt crystallises in well-formed prisms.

γ-Methylphenylparaconic acid, $COOH\cdot CH<\begin{matrix}CH_2\text{---}CO\\ CMePh\cdot O\end{matrix}$, is obtained when γ-methylphenylitaconic acid is heated on the water bath with sulphuric acid diluted with an equal volume of water, or with hydrochloric acid of sp. gr. 1·15; also, when the last-named acid is treated in the cold with hydrobromic acid saturated at 0°. It forms stellate groups of needles, and melts at 123—124°. The *calcium* salt is very sparingly soluble in alcohol, and the *silver* salt is readily soluble in water.

γ-Methylphenyl-β-bromoparaconic acid, $COOH\cdot CBr<\begin{matrix}CH_2\text{---}CO\\ CMePh\cdot O\end{matrix}$, is obtained by brominating γ-methylphenylitaconic acid; it crystallises from benzene in stellate groups of needles, and melts at 152—153° with decomposition; when reduced with sodium amalgam, it is quantitatively converted into γ-methylphenylparaconic acid. *γ-Methylphenylaconic acid*, $COOH\cdot C<\begin{matrix}CH\text{---}CO\\ CMePh\cdot O\end{matrix}$, is formed when the last-described bromo-acid is boiled with water; it crystallises in four-

sided prisms, melts at 178—179°, and is converted into γ-methylphenylparaconic acid when treated with sodium amalgam.

The acid isomeric with γ-methylphenylitaconic acid, obtained in the preparation of the latter (see above), forms needles, melts at 142—143°, and is probably *methylphenylaticonic acid;* it yields a bromolactonic acid, $C_{12}H_{11}BrO_4$, which melts at 175°.

By the action of sodium ethoxide on a mixture of methyl ethyl ketone and diethylic succinate, two isomerides, *γ-methylethylaticonic acid* and *γ-methylethylitaconic acid*, are formed. The latter is produced in the lesser amount, and is less soluble in ether than the former; it melts and decomposes at 165—167°. *γ-Methylethylaticonic acid* melts at 141—142°; the *barium* salt crystallises with $3H_2O$.

γ-Methylethylparaconic acid, $COOH\cdot CH<\begin{matrix}CH_2—CO\\ CMeEt\cdot O\end{matrix}$, is produced when γ-methylethylaticonic acid is heated with dilute sulphuric acid; it crystallises from benzene in prisms, and melts at 125—126°.

γ-Methylethylbromoparaconic acid, $C_8H_{11}BrO_4$, separates from water in monosymmetric crystals. $a : b : c = 1{\cdot}8275 : 1 : 1{\cdot}5087$; $\beta = 41° 13'$, and melts at 160—161°. If reduced with sodium amalgam, it yields γ-methylparaconic acid.

Ethylic hydrogen diphenylitaconate, $COOH\cdot CH_2\cdot C(COOEt):CPh_2$, is obtained by the action of sodium ethoxide on a mixture of benzophenone and diethylic succinate; it is sparingly soluble in water, and melts at 124·5—125·5°. On hydrolysis with alkali, it yields *diphenylitaconic acid*, $COOH\cdot CH_2\cdot C(COOH):CPh_2$, which melts and decomposes at 160°. A. R. L.

Magnesiumdiphenyl. By F. Waga (*Annalen*, 1894, **282**, 320—333).—The author has observed that mercurydiphenyl and magnesium powder may frequently be heated together at 200—210°, as Fleck directs (Abstr., 1893, i, 622), for as long as 40 hours without any action taking place, and that the decomposition commences suddenly without carbonisation when the temperature is raised to 220°. He also finds that, when the temperature is maintained at 200—210°, the addition of a small quantity of mercuric chloride accelerates the commencement of the action. The decomposition proceeds with regularity at 180—185° if the mixture of mercurydiphenyl and magnesium is moistened with a few drops of ethylic acetate. Whereas an addition of mercury and (excess of?) magnesium is without essential influence, that of ammonium chloride and mercury phenyl chloride checks the reaction. When once the action has commenced, it should be carried to the end without intermission. The crude magnesiumdiphenyl must be treated with benzene to remove the mercury compounds with which it is contaminated; a small quantity of diphenyl and metallic mercury are produced in the reaction just described. When either magnesium powder or magnesium amalgam, moistened with ethylic acetate, is heated with diphenyl at 180—185°, no magnesiumdiphenyl is obtained.

Magnesiumdiphenyl reacts with benzoic chloride, forming benzo-

phenone; with acetic chloride, forming acetophenone; with sulphuryl chloride, forming diphenyl; with benzoic sulphochloride, forming diphenylsulphone; with arsenious chloride, forming arsenious phenyl chloride, $AsCl_2Ph$; with stannic chloride, forming stannicdiphenyl chloride, $SnCl_2Ph_2$, which interacts with water, yielding stannicdiphenyl hydroxychloride, $Sn(OH)ClPh_2$; and with chloroform, forming triphenylmethane. In some cases, the reagents are mixed alone; in others the magnesiumdiphenyl is dissolved in a mixture of benzene and ether. The product of the action of magnesiumdiphenyl on carbon tetrachloride consists of a small quantity of triphenylmethane and a dark, resinous substance; whilst a colouring matter, perhaps benzaurin, $OH\cdot CPh:(C_6H_4\cdot OH)_2$, is formed from magnesiumdiphenyl and benzotrichloride. In neither of the last two experiments was the hitherto unknown tetraphenylmethane isolated. A. R. L.

Diphenylsulphone Derivatives. By O. Hinsberg (*Ber.*, 1894, **27**, 3259—3261).—Benzenesulphinic acid reacts with quinones and paranitrosamines in a similar manner to hydrochloric acid (*Ber.*, **19**, 2010).

Paradihydroxydiphenylsulphone, $C_6H_3(OH)_2\cdot SO_2Ph$, prepared from quinone and benzenesulphinic acid, forms colourless prisms which are soluble in alkalis and alkali carbonates. On oxidation, it is converted into the corresponding *quinone*, $C_6H_3O_2\cdot SO_2Ph$, which melts at 196°. The *dibenzoate* crystallises in colourless needles, melting at 186°.

Diphenyldisulphonedimethylparaphenylenediamine,

$$NMe_2\cdot C_6H_2(SO_2Ph)_2\cdot NH_2,$$

is obtained from nitrosodimethylaniline and benzenesulphinic acid; it forms slender, yellow crystals, melting at 223°. Mineral acids produce colourless, crystalline salts, which are decomposed by water. The *acetyl* derivative melts at about 252°. The amine is not acted on by hydrochloric acid at 130—140°. A. H.

Synthesis of Derivatives of Indole and Glycocine. By O. Hinsberg and J. Rosenzweig (*Ber.*, 1894, **27**, 3253—3258; compare Abstr., 1888, 372; 1892, 1458).—Glyoxal sodium hydrogen sulphite reacts in dilute alcoholic solution with primary and secondary amines to form either glycocine or indole derivatives. Of the amines which have been hitherto used, benzylamine, piperidine, aniline, ortho- and para-toluidine, and orthamidobenzoic acid yield glycocine compounds; α- and β-naphthylamine and ethylnaphthylamine form indole derivatives, whilst methylaniline and ethylaniline yield a mixture of the two. The following have been prepared in addition to those previously described. *Orthotoluidoacetic orthotoluidide*,

$$C_7H_7\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

forms white, vitreous plates, melting at 94°, and gives crystalline salts with the mineral acids. Anthranilic acid reacts with the glyoxal solution to form the *dicarboxylic acid* of *anilidoacetanilide*,

$$COOH\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot COOH,$$

which crystallises in colourless needles, melting at 250°, and does not form salts with mineral acids; this is accompanied by *orthocarboxyanilidoacetic acid*, $COOH{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}COOH$, which is soluble in hot water, and crystallises in flat prisms, melting at 207°. The same substance is also formed by the action of anthranilic acid on monochloracetic acid. *Piperidoacetic piperidide*, $C_5NH_{10}{\cdot}CH_2{\cdot}CO{\cdot}C_5NH_{10}$, forms large prisms, and melts at 51°; the *platinochloride* decomposes at 212°.

1″-Ethyl-β-naphthindolesulphonic acid, which has been previously described, forms a *silver salt*, which crystallises from hot water in brown needles, and decomposes at 120°. When a solution of its sodium salt is boiled with an excess of hydrochloric acid, the whole of the sulphur is eliminated, partly in the form of sulphurous anhydride, 1″-*ethylnaphthindole*, $C_{10}H_6{<}^{NEt}_{CH}{>}CH$, being formed; the latter is readily volatile with steam, and crystallises in small, white needles, melting at 73°. It gives the indole reaction, and forms a deep red colouring matter with diazobenzene chloride. *Sodium* 1″-*methylindolesulphonate*, $C_6H_4{<}^{NMe}_{CH}{>}C{\cdot}SO_2Na$, is obtained, together with methylphenylglycocine, when methylaniline is treated with the glyoxal solution; it crystallises from water in white plates, and is not decomposed at 300°. When warmed with hydrochloric acid, it is readily converted into 1″-*methyloxindole*, $C_6H_4{<}^{NMe}_{CH_2}{>}CO$, which crystallises in needles, melting at 89°. The sodium salt of the sulphonic acid reacts with bromine in alkaline solution to form a mixture of two isatins, which are being further investigated. Ethylaniline behaves like methylaniline. A. H.

Tetramethyldiamidobenzhydrol. By H. Weil (*Ber.*, 1894, **27**, 3316—3317).—When this substance is boiled with dilute mineral acids or with acetic acid, it is decomposed into dimethylaniline and dimethylamidobenzaldehyde; the latter, as well as the benzhydrol itself, condenses with the dimethylaniline to form leuco-violet.

Dimethylamidobenzaldehyde forms benzylidene compounds with primary aromatic amines even in acid solutions, a coloration or a coloured precipitate being produced; the reaction is especially delicate with benzidine compounds. C. F. B.

Diphenylmethane Colouring Matters. By K. Albrecht (*Ber.*, 1894, **27**, 3294—3299).—*Tetramethyldiamidodiphenylamidoacetonitrile* or *hydrocyanauramine*, $NH_2{\cdot}C(CN)(C_6H_4{\cdot}NMe_2)_2$, is prepared by the interaction of potassium cyanide and auramine in alcoholic solution at the ordinary temperature; it is deposited in colourless crystals, melts at 130°, and is resolved into hydrogen cyanide and auramine. The yield is 90 per cent. of the theoretical. By the prolonged action of boiling water, or more rapidly with glacial acetic acid or dilute hydrochloric acid, the nitrile is hydrolysed, ammonia is eliminated, and the resulting carbinol, in presence of zinc chloride or sodium chloride, is converted into the chloride, $NMe_2{\cdot}C_6H_4{\cdot}C(CN){:}C_6H_4{:}NMe_2Cl$.

This compound is also formed by the action of nitrites on the nitrile in acid solution, and has been previously obtained by H. Weil (*Ber.*, 1884, **17**, 1403) by the oxidation of tetramethyldiamidodiphenylacetonitrile; it crystallises in green needles, and, in presence of tannin, dyes cotton yellowish-green.

Tetramethyldiamidodiphenylamidoacetamide,

$$NH_2{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}CO{\cdot}NH_2,$$

is prepared by the action of concentrated sulphuric acid on the nitrile at ordinary temperatures; it crystallises in colourless, lustrous needles, and melts at 170°. The yield is 85—90 per cent. of the nitrile employed. The compound is stable, and does not readily react with alcoholic potash or zinc dust; but by the action of acetic acid, the group $CONH_2$ is eliminated; the resulting hydroxy-derivative is greenish-yellow. The *acetamide chloride* is crystalline and colourless.

Tetramethyldiamidodiphenylamidoacetic acid,

$$NH_2{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}COOH,$$

formed by the prolonged action of alcoholic potash on the acetamide, is yellow, crystalline, sparingly soluble, and melts and decomposes at 171°. With nitrous acid, auramine is regenerated. The *hydrochloride* and *sodium salt* are colourless and crystalline, and react with glacial acetic acid like the acetamide.

Tetramethyldiamidodiphenylglycollamide,

$$OH{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}CONH_2,$$

is obtained by the action of hydrochloric acid and zinc chloride on the acetamide; it crystallises with alcohol, and melts at 162—163°; the anhydrous, yellow crystals melt at 140—142°. With tannin as a mordant, it dyes cotton a pure greenish-blue, but the colour is unstable. The basic properties of the compound are feeble; the *salts* dissolve in water with a blue coloration, but soon dissociate. The salts of *tetramethyldiamidodiphenylglycollic acid*, $OH{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}COOH$, are prepared like those of the acetic acid (see above), and by the action of hydrochloric acid and zinc chloride on the amidoacetic acid; the free acid has not been isolated. The *potassium salt* crystallises in colourless, slender needles.

The replacement of hydrogen in tetramethyldiamidodiphenyl carbinol by the CN-, $CONH_2$-, or COOH-groups respectively, causes the colour to change from blue to green and greenish-blue, and its intensity is considerably diminished. J. B. T.

Pyronines. By J. Biehringer (*Ber.*, 1894, **27**, 3299—3305; compare R. Möhlau and P. Koch, this vol., i, 46).—The term pyronine is applied to a class of dyes formed by the condensation of aldehydes (1 mol.) with dialkylmetamidophenols (2 mols.). Dimethylmetamidophenol melts at 85°, readily dissolves in acids and alkalis, and produces mirrors with silver and gold salts. Diethylmetamidophenol resembles the dimethyl derivative, and melts at 74°. The preparation of tetramethyldiamidodihydroxydiphenylmethane from formaldehyde and dimethylmetamidophenol has been previously de-

scribed. The *hydrochloride*, $C_{17}H_{22}O_2N_2,2HCl + H_2O$, crystallises in rose-coloured plates and melts at 110°, the *zincochloride* in needles; the *hydrochloride* of the *benzoyl* derivative crystallises in colourless needles, melts at 141°, and gives a blue coloration with lead peroxide.

Tetramethyldiamidodiphenylmethane oxide, $CH_2:[C_6H_3(NMe_2)]_2:O$, prepared by the action of sulphuric acid on the dihydroxy-derivative, crystallises in lustrous needles or plates, melts at 116°, and is rapidly oxidised by exposure to light. By the prolonged action of the acid on the anhydro-base, a compound is obtained which has a strong blue fluorescence, changing to green on the addition of acid; it is contained in the technical dye, is probably formed by the elimination of the dimethylamine group, and is being further investigated. When oxidised, the anhydro-base yields the carbinol derivative, $OH\cdot CH:[C_6H_3(NMe_2)]_2:O$, which closely resembles rosaniline in appearance. The alcoholic and acetone solutions are red, with a yellow fluorescence; the benzene solution exhibits no fluorescence. The *hydrochloride* crystallises in steel-blue, lustrous needles.

Ethylidenetetramethyldimetamidophenol,

$$CHMe[C_6H_3(NMe_2)\cdot OH]_2,$$

forms colourless crystals melting at 167°, not at 140° as stated by Möhlau and Koch. The *benzoyl* derivative has been prepared, and gives a pale blue coloration with acetic acid and lead peroxide.

J. B. T.

Symmetrical Orthodiamidobenzophenone. By W. Staedel (*Ber.*, 1894, **27**, 3362—3363).—The author has recently shown (Abstr., 1894, i, 599) that the substance usually known as γ-diamidobenzophenone is in reality symmetrical orthodiamidobenzophenone. Since Gram has shown (*Inaug. Diss.*, Jena, 1892) that tetranitrodiphenylmethane is readily converted into symmetrical diamidoacridine, it appeared probable that the above diamido-derivative could in a similar manner be converted into acridine or acridone, and on examination this proved to be the case, although the reactions do not proceed so well as in the case of tetranitrodiphenylmethane. To obtain acridine, the diamido-compound is heated with zinc dust, whilst acridone is formed by heating it with concentrated hydrochloric acid or zinc chloride.

The author has shown in his previous paper that diamidobenzophenone is converted by nitrous acid into xanthone; at the same time an isomeric substance is always obtained, which the author regards as a *hydroxydiphenylene ketone*, $\begin{matrix} C_6H_4 \\ | \\ OH\cdot C_6H_3 \end{matrix}\!\!>CO$, its formation being analogous to that of fluorene from orthamidodiphenylmethane (this vol., i, 52). H. G. C.

Preparation of Orthamidobenzophenone and Synthesis of Acridone. By C. Graebe and F. Ullmann (*Ber.*, 1894, **27**, 3483—3484).—Orthamidobenzophenone is prepared by the action of sodium hypobromite on orthobenzoylbenzamide; the yield is about 40 grams from 50 grams of phthalic anhydride. Attempts to prepare acri-

dine from this by the action of various dehydrating agents were not very successful; the best results were obtained with phosphorus chloride and calcium oxide. Acridone is formed by the action of lead oxide on orthamidobenzophenone at 350—360°; the yield is 50 per cent.

Orthohydroxybenzophenone in small, and fluorenone, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CO$, in large, quantity, are formed from the amidophenone by means of the diazo-reaction. The action is similar to that observed by O. Fischer and H. Schmidt, who prepared fluorene and orthohydroxydiphenylmethane from orthamidodiphenylmethane (this vol., i, 52).

J. B. T.

Condensations with Formaldehyde. By H. Weil (*Ber.*, 1894, **27**, 3314—3316).—When formaldehyde and paranitrotoluene are allowed to remain at the ordinary temperature in solution in strong sulphuric acid, dinitroditolylmethane is formed. This must have the nitro-groups in the meta-position with regard to the CH_2 group, for the only other position possible is the ortho, and this is disproved by the fact that the diamido-compound, which the dinitro-compound yields when reduced with tin and hydrochloric acid, has no tendency to form an acridine. This *diamidoditolylmethane* melts at 98—100°, and yields a *diacetyl* derivative melting at 270°.

Unlike Schöpff (Abstr., 1894, i, 600), the author has found that diphenylmethane-3 : 3′-dicarboxylic acid softens at 240°, and does not melt until 254°.

C. F. B.

Constitution of Fluorindines and Rosindulines. By F. Kehrmann (*Ber.*, 1894, **27**, 3348—3350).—Acetamidonaphthaquinone [O_2 : NHAc = 1 : 2 : 4] (this vol., i, 151) condenses with phenylorthophenylenediamine, yielding two isomeric azonium bases, the hydrochlorides of which have the formula

$$NHAc\cdot C_{10}H_5\!\ll\!\begin{matrix}N\\NPhCl\end{matrix}\!>\!C_6H_4,$$

in which the NHAc- and NPhCl-groups are, for the two isomerides, respectively in the meta- and para-positions. The first loses acetic acid when hydrolysed, with formation of rosinduline hydrochloride, which is therefore a true azonium compound. The relation of induline to safranine is then expressed by the formulæ

$$NH_2\cdot C_{10}H_5\!\ll\!\begin{matrix}N\\NPh(OH)\end{matrix}\!>\!C_6H_4 \qquad NH{:}C_{10}H_5\!\ll\!\begin{matrix}N\\NPh\end{matrix}\!>\!C_6H_4.$$

C. F. B.

Constitution of Safranines. By C. Ris (*Ber.*, 1894, **27**, 3318—3319).—By acting on the indamine, $NH_2\cdot C_6H_4\cdot N{:}C_6H_4{:}NH$, with paramidoacetanilide, an acetylamidosafranine has been prepared, and from this, by hydrolysis, an amidosafranine; these exhibit the same colours as safranine itself. In a similar way an acetylamido- and an amido-dimethylsafranine were prepared, and found to have the same colour as dimethylsafranine. From the fact that the introduction of

a third amido-group produces no change in the colour, it is concluded that Bernthsen's symmetrical formula for safranine (Abstr., 1887, 139) is more probable than the unsymmetrical one proposed by Witt (Abstr., 1887, 250). C. F. B.

Diphenylbenzenes. By L. Olgiati (*Ber.*, 1894, **27**, 3385—3397).—Of the three possible diphenylbenzenes, two are at present known, namely, paradiphenylbenzene, obtained by the action of sodium on a mixture of paradibromobenzene and bromobenzene, and isodiphenylbenzene, the constitution of which is not known with certainty. It has been shown that oxidising agents partially convert it into metadiphenylcarboxylic acid, but as large quantities of paradiphenylcarboxylic acid and terephthalic acid are simultaneously formed, this affords no conclusive proof of its constitution; the author has therefore subjected the iso-compound to a fresh investigation.

For its preparation, benzene vapour was passed through a red-hot tube, and the diphenyl formed at the same time separated by fractional distillation. To separate isodiphenylbenzene from the para-derivative, the alcoholic mother liquors from the crystallisation of paradiphenylbenzene were evaporated, the residue extracted with light petroleum, the latter distilled off, the residue fractionated, and the fraction boiling at 350—400° again subjected to the same treatment. To finally remove the para-compound, the product was dissolved in carbon bisulphide and sufficient bromine added to form the monobromo-derivative, the paradiphenylbenzene remaining unchanged. The monobromisodiphenylbenzene is extracted with light petroleum and treated with sodium amalgam and hot alcohol; on pouring the mixture into water, pure isodiphenylbenzene separates, and, after crystallisation, melts at 84—85°. It gives no trace of paradiphenylcarboxylic acid on oxidation, and is therefore free from the para-compound, whereas the product previously obtained has contained the latter in quantity, thus accounting for the presence of the para-derivatives in the oxidation products. As the subsequent investigation has shown that it is in reality the meta-derivative, the name isodiphenylbenzene need no longer be employed.

Bromometadiphenylbenzene, $C_6H_3Ph_2Br$, is obtained as described above, and forms spherical aggregates of silvery-white needles melting at 31°. On oxidation with chromic acid in acetic acid solution, it is converted into *bromometadiphenylcarboxylic acid*, $C_{12}H_8Br{\cdot}COOH$, which forms small, rhomboidal plates melting at 242°, and may be sublimed; the *barium* salt, with $7\frac{1}{2}H_2O$, is a crystalline precipitate, the *calcium* salt, with $4H_2O$, and the *silver* salt amorphous precipitates. The *methylic* salt, $C_{12}H_8Br{\cdot}COOMe$, forms feathery aggregates of short prisms melting at 67°, and the *ethylic* salt is a syrup. When the acid is treated with zinc dust and soda, it is converted chiefly into metadiphenylcarboxylic acid, thus proving that the diphenylbenzene from which it is derived is in reality the meta-derivative. Attempts to oxidise the bromometadiphenylcarboxylic acid further were not successful, total decomposition taking place; hence it is probable that the bromine atom is combined with the same

nucleus as the carboxyl group, as otherwise bromobenzoic acid would probably have been formed.

By the continued action of bromine on metadiphenylbenzene, it is finally converted into *tetrabromometadiphenylbenzene*,

$$C_6H_3Br_2{\cdot}C_6H_3Br{\cdot}C_6H_4Br,$$

which crystallises in stellate groups of slender plates melting at 181°, and, on oxidation, yields a mixture of bromobenzoic acids, the properties of these agreeing with those of 1 : 3 : 4-dibromobenzoic acid and parabromobenzoic acid.

Parabromoparadiphenylbenzene, $C_6H_4Ph{\cdot}C_6H_4Br$, is prepared by subjecting the hydrocarbon to the action of bromine vapour, and is separated by sublimation from the dibromo-compound simultaneously formed in larger quantity; it crystallises in lustrous plates melting at 228°, and, on oxidation with chromic acid in acetic acid solution, yields *parabromodiphenylcarboxylic acid*, $C_6H_4Br{\cdot}C_6H_4{\cdot}COOH$, which crystallises in small needles, and may be sublimed; on reduction, it yields paradiphenylcarboxylic acid. *Diparabromoparadiphenylbenzene*, $C_6H_4Br{\cdot}C_6H_4{\cdot}C_6H_4Br$, is obtained together with the monobromo-derivative, and is a heavy, white, crystalline powder melting at 304°. On oxidation, it yields parabromobenzoic acid in quantity, the central nucleus being destroyed, with formation of two molecules of the acid. Several salts of parabromobenzoic acid were prepared; the *lead* salt crystallises from boiling water in lustrous plates, the *cadmium* and *copper* salts are crystalline precipitates, and the *methylic* salt, $C_6H_4Br{\cdot}COOMe$, forms volatile plates, having an odour resembling aniseed, and melting at 74°.

Tetrabromoparadiphenylbenzene, $C_6H_4Br{\cdot}C_6H_2Br_2{\cdot}C_6H_4Br$, obtained by treating paradiphenylbenzene or either of the above bromo-derivatives with an excess of bromine, crystallises in long, very thin needles melting at 245°; on oxidation, it is converted into parabromobenzoic acid, but the yield is very poor. H. G. C.

Thio-derivatives of β-Naphthol. By G. Tassinari (*Ber.*, 1894, **27**, 3238).—In connection with the recent paper of Henriques on the above subject (this vol., i, 103) the author points out that he has already studied the action of the chlorides of sulphur on phenol and its homologues, and has obtained several of the compounds described by the former (Abstr., 1887, 807; 1889, 245). H. G. C.

Thio-derivatives of β-Naphthol. By M. Schiller-Wechsler (*Ber.*, 1894, **27**, 3448—3449).—The substances described by Henriques (this vol., i, 103) as dihydroxydinaphthylic sulphide and dehydrodihydroxydinaphthylic sulphide seem to be identical with compounds, for the manufacture of which the author holds a patent (German patent, 64,816). Thiodinaphthylic oxide, identical with the dehydro-compound of Henriques, is used in certain skin diseases, and is at present being further investigated. A. H.

Naphthazarin and the Formation of Naphthocyamic acid. By E. Schunck and L. Marchlewski (*Ber.*, 1894, **27**, 3462—3465).—

The authors have been able to confirm Liebermann's view that naphthazarin is a dihydroxy-α-naphthaquinone, the hydroxyl groups having the position 1′ : 2′. When naphthazarin is boiled with acetic anhydride, sodium acetate, and zinc dust, *tetracetyldihydroxy-α-naphthaquinol*, [$(OH)_4 = 1 : 4 : 1' : 2'$], is produced. It crystallises in flat, almost colourless prisms, and melts at 277—279°. The corresponding tetrahydroxy-compound could not be isolated. The *dioxime* of *naphthazarin* crystallises in brownish needles, which, when heated, decompose before melting.

Naphthocyamic acid is formed by the action of potassium cyanide on β-dinitronaphthalene, and cannot be obtained from the corresponding α-compound. A. H.

Quinoneimides and Amidoquinones. By F. Kehrmann (*Ber.*, 1894, **27**, 3337—3347).—When amidonaphthaquinonimide,

[$O : NH_2 : NH = 1 : 2 : 4$],

is boiled with water containing some ammonia, it yields hydroxynaphthaquinonimide, [$O : OH : NH = 1 : 2 : 4$], together with a little amidonaphthaquinone, [$O : NH_2 : O = 1 : 2 : 4$], which is found to be identical with the amidonaphthaquinone of Meerson (Abstr., 1888, 1200); the latter crystallises in red needles and melts at 202—203°. If, however, its hydrochloride is heated with acetic anhydride and sodium acetate, the acetamido-derivatives of the 1 : 2- and 1 : 4-quinones are formed; the latter, under these circumstances, in larger amount.

When hydroxynaphthaquinonimide, [$O : OH : NH = 1 : 2 : 4$], is reduced with stannous chloride, it yields the readily oxidisable *amidonaphthaquinol*, [$(OH)_2 : NH_2 = 1 : 2 : 4$]. This forms a *triacetyl*-derivative, [$(OAc)_2 : NHAc = 1 : 2 : 4$], melting at 193°, which, on partial hydrolysis with caustic soda, yields the readily oxidisable *acetamidonaphthaquinol*, [$(OH)_2 : NHAc = 1 : 2 : 4$], which is oxidised by chromic mixture to red *acetamidonaphthaquinone*, [$O_2 : NHAc = 1 : 2 : 4$]. With orthophenylenediamine, this yields an *acetamidonaphthaphenazine* which crystallises in yellow needles and melts above 370°; it also yields a red *monoxime* (?).

Amidonaphthaquinone, [$O_2 : NH_2 = 1 : 4 : 2$], undergoes a similar series of changes. When reduced it yields the readily oxidisable *amidonaphthaquinol*, [$(OH)_2 : NH_2 = 1 : 4 : 2$]; this yields a *triacetyl*-derivative, [$(OAc)_2 : NHAc = 1 : 4 : 2$], melting at 259—260°, which, on partial hydrolysis, yields *acetamidonaphthaquinol*, [$(OH)_2 : NHAc = 1 : 4 : 2$], readily oxidisable to yellow *acetamidonaphthaquinone*, [$O_2 : NHAc = 1 : 4 : 2$]; this melts at 202°, and yields a yellow *monoxime*, [$O : NHAc : NOH = 1 : 2 : 4$], decomposing at 195—200°. C. F. B.

Preparation of 1 : 4-Naphtholsulphonic acid. By F. Reverdin (*Ber.*, 1894, **27**, 3458—3462).—The direct sulphonation of α-naphthol invariably leads to the formation of mixtures of sulphonic acids. On the other hand, α-naphthylic carbonate, when sulphonated at a temperature of 10—20°, yields a disulphonic acid which is readily converted into 1 : 4-naphtholsulphonic acid when its solution in water is boiled. If the temperature during sulphonation rises above

20°, the disulphonaphthylic carbonate begins to decompose with formation of naphtholsulphonic acid, which at once undergoes further sulphonation. This method of preparation has been patented and is of great commercial value. Naphthylic carbonate (Burkard, *Inaug. Diss.*, Basel, 1889) is prepared by passing phosgene into a solution of naphthol in aqueous soda. It crystallises in prisms and melts at 130°. A. H.

Orientation in the Terpene Series. By A. Baeyer (*Ber.*, 1894, **27**, 3485—3498).—Carone, like menthone, combines with nitrosyl chloride, forming a tertiary nitroso-derivative; this is not in harmony with the constitution previously suggested (Abstr., 1894, i, 535), according to which it contains a para-linking; it is probable, therefore, that it contains a trimethylene ring, and its behaviour towards hydrogen bromide and potassium permanganate are equally consistent with this view. The formula $C_3H_7\cdot CH<\begin{matrix}CH\cdot CH_2\\ |\\ CH\cdot CO\end{matrix}>CHMe$ is suggested provisionally; it will be fully discussed in a subsequent paper. *Caroneoxime* is an oily liquid, stable towards potassium permanganate, and readily soluble in alkalis and acids. *Carylamine*, $C_{10}H_{19}N$, prepared by reduction of the oxime, has no characteristic odour, is stable towards potassium permanganate, and gives no precipitate with platinic chloride. The *hydrochloride* is crystalline, and is converted into the salt of an isomeric base when warmed in aqueous solution. The *benzoyl* derivative crystallises in large, flat prisms melting at 123°. Cyanic acid and phenylic cyanate yield resinous products; phenylthiocarbimide gives a crystalline compound melting at 145—146°.

Vestrylamine is formed by heating carylamine hydrochloride in dilute aqueous or alcoholic solution; it resembles carylamine, but readily reduces potassium permanganate solution. The *hydrochloride* is crystalline; the *benzoyl* derivative resinous. Judging from the change produced in carone by heating or by the action of sulphuric acid, vestrylamine should be the amine of carveol; attempts to prepare this compound for comparison by reduction of carveoloxime were unsuccessful; it is, however, different from dihydrocarvylamine, and from *dihydroeucarvylamine*, which is an oily liquid that readily reduces potassium permanganate. The *hydrochloride* is crystalline; the *benzoyl* derivative crystallises in long needles melting at 155—156°. The *platinochloride* is sparingly soluble; the cyanic acid and phenylthiocarbamide derivatives are resinous. Vestrylamine hydrochloride yields a hydrocarbon when distilled in a current of hydrogen chloride, whilst carylamine hydrochloride volatilises for the most part without change, but a little of it is converted into vestrylamine hydrochloride, which then decomposes. The crude hydrocarbon gives the sylvestrene reaction, and by means of chromic acid, or, better, with hydrogen bromide in glacial acetic acid it can be separated into two portions. The crystalline compound is *carvestrene dihydrobromide*, $C_{10}H_{16},2HBr$; it crystallises in rhombic plates and melts at 48—50°. The *dihydrochloride* crystallises from glacial acetic acid in long prisms melting at 52·5°.

Carvestrene, prepared by the action of quinoline on the hydrobromide, boils at 178° (corr.), smells like dipentene, becomes resinous on exposure to air, decolorises potassium permanganate solution instantaneously, and is oxidised by chromic acid at ordinary temperatures. As it has no rotatory power in chloroform solution, and gives the sylvestrene reaction, it is probably a mixture of equal molecules of *l*- and *r*-sylvestrene, and bears the same relation to *l*-sylvestrene as dipentene does to *l*-limonene; its boiling point, and the fact that the dihydrobromide and dihydrochloride have different melting points, indicates that it is not a racemic compound. The constitution of carvestrene has not yet been determined with certainty. This series of compounds is divisible into two classes—those which, like carvestrene and terpinene, are readily oxidised, but combine slowly with hydrogen bromide, and those which oxidise with difficulty but yield immediately additive compounds with hydrogen bromide, such as limonene and terpinolene; as the latter compound contains two separated double linkings, the members of the first class probably have the doubly-linked carbon atoms adjacent. It is pointed out that the author and Wallach are agreed that in dipentene the double linkings are in the positions $\Delta^{1,3}$ or $\Delta^{1,4}$, from which it follows that a terpene may be optically active even in the absence of an asymmetrical carbon atom (compare Abstr., 1894, i, 252).

W. F. Proost's recent paper on the resolution of $\Delta^{2,6}$-dihydrophthalic acid into active components (this vol., i, 141) is also referred to; and although this result alone is insufficient to cause the rejection of the formula, the preparation of the acid by intramolecular rearrangement from the acid $\Delta^{3,5}$ is equally compatible with the intermediate constitution $\Delta^{3,6}$, which contains an asymmetric carbon atom; should further investigations confirm this suggestion, the striking similarity of the compound, in chemical properties, to the acid $\Delta^{2,4}$ will be satisfactorily explained. The orientation in the phthalic acid series is by no means so well established as in the terephthalic acid derivatives, as, owing to the great instability of many of the former compounds, several members have not yet been isolated.

J. B. T.

Hydroxyterpenylic acid. By O. Best (*Ber.*, 1894, **27**, 3333—3335).—A reply to some criticisms of Wallach (Abstr., 1894, i, 421).

Pennyroyal Oil. By T. am Ende (*Chem. Centr.*, 1894, i, 743).—The chief constituent of the essential oil of pennyroyal is the ketone, $C_{10}H_{16}O$, pulegone. Besides the oxime-like compound (m. p. 157°) obtained by Beckmann (Abstr., 1891, 936) by the action of hydroxylamine on pulegone, the normal *pulegoneoxime*, m. p. 118—119°, is obtained by adding hydroxylamine hydrochloride and alkali to an alcoholic solution of pulegone. Pulegoneoxime, when treated with dilute acids, does not yield a nitrile, but is reconverted into pulegone, and it remains unchanged when treated with phosphoric anhydride or phosphorus pentachloride. A liquid *oxime* is obtained, along with the above pulegoneoxime. *Pulegoneamine* is formed when the oxime is reduced with sodium and alcohol; it melts at 49—50°, the *oxalate* melts at 109—110°. The liquid pulegoneoxime, on reduction, yields a

mixture of the pulegoneamine, melting at 49—50° and boiling at 205—210°, and an *amine* which boils at 205—210°. Pure pulegone is obtained by decomposing pulegoneoxime with dilute sulphuric acid; it boils at 220—225°, has the refractive index $n_D = 1{\cdot}47974$ at 21°, and the sp. gr. = 0·933 at 20°.

Wallach (Abstr., 1893, i, 115) has obtained two bases, boiling at 160—170° and 250° respectively, by treating pennyroyal oil with ammonium formate. The author has obtained the same bases by the action of ammonium formate on pulegone. The base of lower boiling point, which boils at 150—151°, was identified as heptyleneamine, $C_7H_{13}{\cdot}NH_2$, and was converted into a carbamide, melting at 173°. The base of higher boiling point, $NH(C_7H_{13})_2$, is the secondary base corresponding with heptylamine; it boils at 275°, and solidifies in a freezing mixture. E. C. R.

Preparation of Bromocamphoric Anhydride and of Lauranolic acid. By O. Aschan (*Ber.*, 1894, **27**, 3504—3508).—The unsaturated acid, obtained by the action of alkali on bromocamphoric anhydride (Abstr., 1894, i, 615), proves to be lauranolic acid; it was identified by means of the calcium and silver salts, and by the preparation of the *amide*, which crystallises in hydrated, highly-lustrous plates, melting at 72°. The *bromolactone*, $C_9H_{13}BrO_2$, smells like camphor and melts at 187°. Details of an improved method for the preparation of bromocamphoric anhydride are given, by which the yield is increased from 50 to 70 per cent.; the chief difference from the method already described is that only slightly more than the theoretical quantity of bromine is employed. The yield of lauranolic acid is 17 per cent. of the bromanhydride taken, in addition to the camphanic acid; the latter is converted directly into lauranolic acid by distillation under reduced pressure; the yield is about 24 per cent. together with 5 per cent. of campholactone and 10 per cent. of a hydrocarbon, C_8H_{14}, previously obtained by Wreden by heating camphanic acid with water. The relative proportions in which the three compounds are formed is largely dependent on the pressure under which the distillation is conducted; increase in this diminishes the quantity and purity of the lauranolic acid. J. B. T.

Sulphocamphylic acid. By W. Koenigs and C. Meyer (*Ber.*, 1894, **27**, 3465—3470).—Sulphocamphylic acid crystallises with $3H_2O$, two of which are lost at 100°. The third molecule is lost at 106—108°, so that the anhydrous acid has the formula $C_9H_{14}SO_5$. The *normal methylic salt* melts at 72°, the *monomethylic salt* at 140°. They are both formed when the normal silver salt is heated with methylic iodide and benzene under an additional pressure of a few centimetres of mercury.

Isolauronolic acid, which is obtained when sulphocamphylic acid is treated with superheated steam, is converted, by careful oxidation with permanganate, into *isolauronic acid*, $C_9H_{12}O_3$. This substance crystallises from hot water in yellow needles, and melts at 132°. The acid is monobasic, and forms a sparingly soluble, crystalline, *silver salt*. It contains a keto- or aldehyde-group, and reduces am-

moniacal silver oxide even in the cold. The *phenylhydrazine* compound crystallises in yellow needles, and melts at 199°; the *semicarbazide* compound is a white, crystalline precipitate, which melts and decomposes at 248—250°. When this acid is heated on the water bath with sulphuric acid, it is converted into paraxylylic acid, $C_9H_{10}O_2$.

When sulphocamphylic acid is heated at 170—180° with aqueous phosphoric acid, it yields the same hydrocarbon of the formula C_8H_{14} as has already been obtained by Damsky by the distillation of ammonium sulphocamphylate with ammonium chloride. A. H.

Synthesis of Quinoline and of Scatole. By E. Bamberger and M. Kitschelt (*Ber.*, 1894, **27**, 3421—3427).—When the ethyl ether of monophenylglycoline is treated with phosphoric anhydride, a mixture of quinoline, scatole, and aniline is formed, accompanied by a secondary base, which is probably 1′ : 4′-dihydroquinoline.

Phenylglycoline ethyl ether, $NHPh{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OEt$, is prepared by warming a mixture of formanilide and dichlorhydrin in alcoholic solution with sodium ethoxide. It crystallises from light petroleum in rhombic plates, which become bluish-violet on exposure to air; it melts at 61·5°, and boils at 217° under a pressure of 40 mm. A brownish-green coloration is developed in the acid solution by potassium dichromate and by ferric chloride. The *acetyl* derivative, which is formed with elimination of $2H_2O$, is a pale yellow, viscous oil; the *nitrosamine* is also an oil.

Phenylglycoline, $NHPh{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, is obtained on hydrolysing the ethyl ether with concentrated hydrochloric acid at 150—155°. It melts at 52° and boils at 249° (50 mm.). The solution in sulphuric acid is coloured brownish-green by potassium dichromate, whilst ferric chloride develops a yellowish-brown coloration. The *acetyl* derivative is a yellowish oil, and the *benzoyl* derivative crystallises in lustrous plates, which melt at 113°. When heated with zinc chloride at 230°, phenylglycoline yields a mixture of the above-mentioned bases. M. O. F.

Constitution of the so-called Quinoline Ammonium Bases. By W. Roser (*Annalen*, 1894, **282**, 363—373, 373—385).—The experiments recorded in these papers were made to test the author's speculations (Abstr., 1893, i, 177). When the methochloride of cinchonic acid is dissolved in concentrated sodium hydroxide, two compounds are formed, to which the author assigns the names methyldihydrocinchonic acid and methylquinolonecarboxylic acid. The alkaline solution is nearly neutralised with hydrochloric acid and acetic acid added to the filtrate until a precipitate no longer falls; this precipitate is *methyldihydrocinchonic acid*, $C_6H_4<\begin{matrix}C(COOH):CH\\ NMe\text{——}CH_2\end{matrix}$; it crystallises from aqueous alcohol in minute, yellow needles, has not a sharp melting point, and dissolves in hydrochloric acid, forming a colourless solution, from which it is reprecipitated by sodium carbonate, but is redissolved by an excess of that reagent, forming a

yellow solution. The compound decomposes when kept, becoming brownish-red, and is then no longer soluble in alkalis.

Methylquinolonecarboxylic acid, $C_6H_4<\begin{matrix}C(COOH):CH\\ NMe\text{ ——}CO\end{matrix}$, is precipitated on adding hydrochloric acid to the filtrate from the last compound; it melts at 246°, and is colourless when pure. The author regards this acid as identical with the so-called methylenecinchoxinic acid (Claus, Abstr., 1892, 1490). When the silver salt is distilled in a current of hydrogen, a compound passes over, which is probably methylquinolone.

When quininic acid methochloride is dissolved in alkali, a yellowish-red solution is formed, from which hydrochloric acid precipitates *paramethoxymethylquinolonecarboxylic acid*, $C_{12}H_{11}NO_4$, which forms yellow needles, and melts above 290°; the other product of the reaction was not investigated. The author then discusses the bearing of these results on his theoretical views.

α-Iodoquinoline methiodide, C_9NH_6I,MeI, is prepared by heating α-chloroquinoline with excess of methylic iodide in a sealed tube at 100°; it gives a *compound*, $C_{10}NH_9I_2$,$C_{10}NH_9I{\cdot}OEt$, which melts at 80—82°, and crystallises in brown needles, having a metallic lustre. The question whether a complete conversion into α-ethoxyquinoline methoxide is possible was not answered.

α-Iodoquinoline ethiodide, C_9NH_6I,EtI, crystallises from alcohol in brown needles and melts at 220°; it reacts vigorously with aniline, forming *α-phenylamidoquinoline methiodide*, $C_9NH_6{\cdot}NHPh,MeI$, which forms yellow, lustrous crystals and melts at 118—119°; the corresponding *methochloride* melts at 99°, and forms a crystalline platinochloride.

α-Phenylhydrazidoquinoline methiodide, $C_9NH_6{\cdot}N_2H_2Ph,MeI$, is formed by treating α-iodoquinoline methiodide with phenylhydrazine; it melts at 230°; the corresponding *methochloride* becomes dark at 150°. These derivatives are closely related to those described by Epharüm (Abstr., 1891, 1509).

α-Amidoquinoline methiodide, $C_9NH_6{\cdot}NH_2,MeI$, is obtained by heating α-iodoquinoline methiodide with alcoholic ammonia; it melts at 247°, and the *acetyl* derivative, $C_9NH_6{\cdot}NHAc,MeI$, melts at 213°. The *methochloride* melts at 268°, and yields a *platinochloride* melting at 268° and a mercurochloride melting at 163—165°.

α-Amidoquinoline ethiodide, $C_9NH_6{\cdot}NH_2,EtI$, melts at 232°.

The *benzenylamidoxime*, $CH<\begin{matrix}CH\cdot C\cdot N:CPh\\ C_6H_4{\cdot}NMe{\cdot}O\end{matrix}$, is obtained by shaking α-amidoquinoline methochloride with benzoic chloride and an alkali; it melts at 134—135°. The *hydrochloride* melts at 198°, and the *sulphate* melts at 230°.

α-Methylamidoquinoline methiodide, $C_9NH_6{\cdot}NHMe,MeI$, is obtained by treating amidoquinoline methoxide with methylic iodide; it crystallises with $1H_2O$ in long needles, and, after crystallisation from alcohol, melts at 160°. The corresponding *methochloride* yields a crystalline *platinochloride*.

Dimethylamidoquinoline methiodide, $C_9NH_6{\cdot}NMe_2,MeI + H_2O$,

crystallises in radiating groups of needles, and melts at 197°; when boiled with sodium hydroxide, it yields dimethylamine and methylquinoline. A. R. L.

Derivatives of Citrazinamide: Configuration of Aconitic acid. By S. Ruhemann and K. J. P. Orton (*Ber.*, 1894, **27**, 3449—3457).—The homologues of aniline react with citrazinamide in a similar manner to aniline itself. *Diorthotoluidocitrazinamide*, $C_{20}H_{18}N_4O_3$, forms chocolate-brown crystals, whilst *dixylidocitrazinamide*, $C_{22}H_{22}N_4O_3$, is a red precipitate.

Phenylhydrazine, on the other hand (Abstr., 1894, i, 260), only removes 2 atoms of chlorine, a compound of the formula

$$NH_2\cdot CO\cdot C\begin{matrix}<\\>\end{matrix}\begin{matrix}CCl\text{———}C(OH)\\C(N\cdot NHPh)\cdot CO\text{———}\end{matrix}\begin{matrix}>\\<\end{matrix}N,$$

being formed.

Trichlorocitrazinamide dissolves in alcoholic ammonia with formation of an ammonium salt. When reduced with alcoholic ammonium sulphide, it is converted into *dihydrodichlorohydroxycitrazinamide*, $NH_2\cdot CO\cdot CH<\begin{matrix}CCl_2\text{———}CO\\CH(OH)\cdot C(OH)\end{matrix}>N$, which crystallises in colourless needles and decomposes at 98°. The *ammonium* salt of this substance forms yellowish needles, whilst the *aniline* salt also forms yellow needles, decomposing at 135°.

When dihydrodichlorohydroxycitrazinamide is treated with phenylhydrazine, a salt of the formula $C_6H_6Cl_2N_2O_4,NH_2\cdot NHPh$, is formed, which crystallises in yellow needles and decomposes at 145°; when this is boiled in aqueous solution with phenylhydrazine and a little acetic acid, a phenylhydrazine salt of the formula

$$OH\cdot\underset{\|}{C}\cdot C(N_2HPh)\cdot\underset{\|}{C}\cdot CO\begin{matrix}>\\\end{matrix}N$$
$$\underset{}{N\cdot CO\text{———}C\cdot NH}$$

is formed. It crystallises in reddish-brown needles, and when boiled with glacial acetic acid, a new compound, $C_{18}H_{13}N_5O_3$, is produced, which is the *phenylhydrazone* of *phenylpyrazolonediketohydroxypyridine*; this crystallises in red needles, decomposes at 245°, and does not reduce Fehling's solution. It is probable that when dihydrodichlorohydroxycitrazinamide is treated with phenylhydrazine, an intermediate compound of the formula $NHPh\cdot N{:}C<\begin{matrix}C(CONH_2){:}CCl\\C(OH)\text{=}\text{=}\text{=}N\end{matrix}>CO$ is formed. The remaining chlorine atom is then replaced by the phenylhydrazine residue, ammonia is evolved, and the phenylhydrazine salt described above is formed. The phenylhydrazone, $C_{18}H_{13}N_5O_3$, is not altered by treatment with hydrochloric acid, but is converted by aqueous potash into a colourless substance, $C_{18}H_{12}N_4O_4$, which crystallises in needles, melting at 245° with evolution of gas. This compound is probably *phenylpyrazolonephenylpyridazonecarboxylic acid*, $\begin{matrix}N{:}C(COOH)\cdot\underset{\|}{C}\cdot CO\\NPh\cdot CO\text{——}\underset{}{C\cdot NH}\end{matrix}>NPh$.

Of the two possible configurations, I and II, aconitic acid seems to

have the first, as this alone can be reconciled with the formation of citrazinamide from it.

I. $\begin{matrix} COOH\cdot C\cdot H \\ \| \\ COOH\cdot CH_2\cdot C\cdot COOH \end{matrix}$. II. $\begin{matrix} H\cdot C\cdot COOH \\ \| \\ COOH\cdot CH_2\cdot C\cdot COOH \end{matrix}$.

The fact that trichlorocitrazinamide does not form a pyrazolone derivative when treated with phenylhydrazine, is also in favour of this view. The second, maleïnoid, formula probably represents the constitution of aceconitic acid (Baeyer, *Annalen*, 1865, **135**, 306).

The formation of a pyrroline derivative from aconitic acid must be supposed to take place indirectly, transformation into the maleïnoid form preceding the closing of the pyrroline ring (Trans., 1894, 9).

A. H.

Scopolamine. By E. SCHMIDT (*Arch. Pharm.*, 1894, **232**, 409—437).—In a former communication (Abstr., 1892, 1255), the author showed that the so-called commercial hyoscine preparations consisted chiefly of a base of the formula $C_{17}H_{21}NO_4$, to which he gave the name scopolamine. As Ladenburg called this work in question (Abstr., 1892, 1366), the author has again examined samples of commercial hyoscine bromide and hyoscine iodide, but in all cases has found them to consist mainly of the corresponding scopolamine salt, together with traces of salts of atropine and hyoscyamine and of another alkaloïd present in too minute traces for characterisation. The author has also investigated large quantities of hyoscyamus seeds. Considerable quantities of scopolamine and hyoscyamine and small quantities of atropine were obtained from these seeds, but no hyoscine could be detected. He therefore considers the existence of hyoscine, $C_{17}H_{23}NO_3$, to be doubtful, although not yet fully disproved.

Scopolamine picrate crystallises in yellow needles melting at 187—188°, and soluble in boiling water. The *methiodide* forms colourless prisms melting at 215°, and easily soluble in water and boiling alcohol. The methiodide is not decomposed by potash, but, with moist silver oxide, yields the *methohydroxide* as a strongly alkaline, gummy, and hygroscopic mass; this reaction proves scopolamine to be a tertiary base. The *methaurochloride* forms yellow, silky needles melting at 145—146°. *Scopolamine ethiodide* forms colourless needles melting at 185—186°. *Benzoylscopolamine hydrochloride*, $C_{17}H_{20}BzNO_4,HCl$, was obtained as a syrup, from which the *aurochloride* was prepared as an amorphous salt melting at 161°, the *platinochloride* as an amorphous salt melting at 199—200°.

Acetic chloride is without action on either hyoscyamine or atropine, but benzoic chloride reacts with both these alkaloïds. With atropine, it yields *benzoylatropine;* with hyoscyamine, according to the conditions of experiment, *benzoylhyoscyamine* or benzoylatropine. *Benzoylhyoscyamine aurochloride*, $C_{17}H_{22}BzNO_3,HAuCl_4$, is a yellow, amorphous mass melting at 70°; the corresponding *platinochloride* melts at 164—170°. *Benzoylatropine aurochloride*, $C_{17}H_{22}BzNO_3,H,AuCl_4$, is a yellow, amorphous, and gummy mass melting at 125—135°; the corresponding *platinochloride* melts at 215°. When hyoscyamine or

atropine is heated with acetic anhydride and a little sodium acetate, no acetylisation occurs, but both the alkaloïds are converted, by the abstraction of the elements of water, into apoatropine. Under like conditions, scopolamine appears to be partly acetylated, partly converted into an apo-derivative, but the products could not be fully isolated. When an aqueous solution of scopolamine hydrobromide is treated with moist silver oxide, it is in part converted into an almost *inactive scopolamine*, which crystallises (more easily than the ordinary scopolamine) in needles melting at 55—56°, and yields an *aurochloride* closely resembling that of the ordinary alkaloïd. The *hydrobromide* is much more readily crystallisable than that of the normal alkaloïd, and forms colourless, crystalline aggregates, showing a rotation $[\alpha]_D = +0{\cdot}44°$ as compared with $[\alpha]_D = -25°\ 43'$ for normal scopolamine hydrobromide. This inactive scopolamine is still under investigation.

Scopoline, which is now being investigated, is a tertiary base, which is oxidised by barium permanganate to a secondary base, $C_7H_{11}NO_2$; the latter yields a crystalline *nitroso*-derivative, but is reconverted into scopoline by the action of methylic iodide.

L. T. T.

Identity of Sophorine and Cytisine. By P. C. Plugge (*Arch. Pharm.*, 1894, **232**, 444—460).—Considerable quantities of sophorine were extracted from *Sophora tomentosa*, and very carefully compared with pure cytisine, $C_{11}H_{14}N_2O$, with the result that these two alkaloïds proved to be identical. During this investigation, many new characteristics of cytisine were determined, and new derivatives formed.

The rotary polarisation of cytisine nitrate is $[\alpha]_D = -93°\ 26'$, the coefficient of refraction, 1·34449. Cytisine gives no reaction with strong sulphuric acid, or with that acid and sugar, cerous oxide, or vanadic acid. Fröhde's reagent, and evaporation with phosphoric acid, likewise yield no reaction. Erdmann's reagent causes an orange-yellow coloration; concentrated nitric acid, on warming, a reddish-yellow coloration, which becomes rather darker on the addition of potash; strong sulphuric acid and potassium dichromate, a green coloration; evaporation with hydrochloric acid leaves a yellow residue; calcium hypochlorite gives no coloration.

Methylcytisine hydriodide, $C_{12}H_{16}N_2O,HI$, prepared by the action of methylic iodide on the free alkaloïd, yields colourless crystals; its solution gives a rotary polarisation, $[\alpha]_D = -81°$, and a refractive index of 1·35427. The *platinochloride* crystallises in orange-yellow needles; the *aurochloride* in golden-yellow needles.

With bromine, cytisine yields an orange-red compound containing 4 atoms of bromine, 2 of which are removed by digesting it with silver nitrate. The compound probably has the formula

$$C_{11}H_{12}N_2OBr_2,2HBr.$$

The author claims priority for his pupil, van de Moer, in establishing the identity of sophorine with cytisine.

As both ulexine and sophorine are now proved to be identical with cytisine, this alkaloïd has been shown to be present in the various

species of *Cytisus*, in *Ulex europæus*, and in *Sophora tomentosa*. Haage and Schmidt failed to find it in *S. japonica*, *S. jap. pendula*, and *S. affinis*, but it is probably present in the poisonous species *S. speciosa* and *S. secundiflora*. L. T. T.

Alkaloïds from the Rind of Pomegranate Root. By G. Ciamician and P. Silber (*Ber.*, 1894, **27**, 2850—2861; compare Abstr., 1894, i, 154).—Norgranatanine (*loc. cit.*) is best obtained by heating granatoline with phosphorus and hydriodic acid for 6—8 hours at 260°, and is separated by means of the carbamate, which melts at 135—136°; the base forms colourless needles melting at 50—60°, and the *platinochloride* separates in yellow plates which melt at 255°. The *nitroso*-derivative, $C_8H_{14}N{\cdot}NO$, melts at 148°. The *benzoyl* derivative forms colourless needles, which melt at 111°. When the dry hydrochloride is distilled with excess of zinc dust, α-propylpyridine is formed, the behaviour of norgranatanine under these circumstances being identical with that of γ-coniceïne.

Norgranatoline, $C_8H_{15}NO$, is obtained by the oxidation of granatoline with potassium permanganate in alkaline solution; it crystallises in needles or colourless prisms, and melts at 134°. The *hydrochloride* is hygroscopic, and the *aurochloride* melts at 215°. The *nitroso*-derivative forms colourless plates, which retain water and melt at 72—73°; in the anhydrous condition it melts at 125°. Pyridine is produced by the distillation of norgranatoline hydrochloride with zinc dust.

Norgranatenine, $C_8H_{13}N$, is formed on reducing norgranatoline with phosphorus and hydriodic acid. The *carbamate* melts at 104—106°, the *hydriodide* at 221°, the *hydrochloride* at 250°, and the *aurochloride* at 186°. The *platinochloride* crystallises in reddish-yellow plates, which do not melt below 260°.

The probable constitutions of some of these substances are also discussed. M. O. F.

A New Decomposition Product of Keratin. By S. G. Hedin (*Zeit. physiol. Chem.*, 1894, **20**, 186—192).—By methods similar to those employed by Drechsel in the preparation of lysine and lysatinine, a new base of the formula $C_6H_{14}N_4O_2$ was obtained from horny substances; it has the same formula, and is probably identical with arginine, prepared by Schulze and Steiger from etiolated lupin seedlings. The following compounds were prepared in a crystalline form. (1) $AgNO_3,C_6H_{14}N_4O_2 + \frac{1}{2}H_2O$; (2) $AgNO_3,C_6H_{14}N_4O_2,HNO_3$; (3) $C_6H_{14}N_4O_2,HNO_3 + \frac{1}{2}H_2O$; and (4) $Cu(NO_3)_2,2C_6H_{14}N_4O_2 + 3H_2O$. W. D. H.

Organic Chemistry.

Methyltrimethylene. By N. Demyanoff (*Ber.*, 1895, **28**, 21—24).—β-Butyleneglycol was prepared by reducing aldol with sodium amalgam; it was then converted, by treatment with hydrobromic acid, into dibromobutane, $CHMeBr{\cdot}CH_2{\cdot}CH_2Br$, and this was heated with zinc dust and alcohol, when *methyltrimethylene*, $CHMe<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, was formed. This is a gas which burns with a smoky flame; it can be condensed to a liquid, which boils at 4—5°, and has sp. gr. = 0·6912 at −20°/0°, = 0·6760 at −8°/20°. It does not decolorise permanganate, nor does it unite with bromine in the dark; in diffused light it unites slowly with bromine, in direct sunlight instantaneously, forming the above-mentioned dibromobutane. It unites with concentrated hydriodic acid, forming secondary iodobutane; concentrated sulphuric acid absorbs and polymerises it, but the dilute acid (1 : ½ of water by vol.) converts it, in part, at least, into butylic alcohol.

The compounds $Br{\cdot}[CH_2]_4{\cdot}Br$, $Br{\cdot}[CH_2]_5{\cdot}Br$, and

$$CHMeBr{\cdot}[CH_2]_4{\cdot}Br,$$

when treated with zinc dust and alcohol, behave in a different way, and yield monobromo-derivatives of the hydrocarbons.

C. F. B.

Reduction of solid α-Dichloroethylic Cyanide. By J. Troeger (*J. pr. Chem.*, 1894, [2], **50**, 446—460).—The author has re-examined the reduction of solid α-dichloroethylic cyanide, which was first investigated by Otto and Voigt (Abstr., 1887, 1024). The first product of reduction is trimolecular *monochlorethylic cyanide*, $(CHMeCl{\cdot}CN)_3$, an oil which decomposes when distilled, but is slowly volatile with steam. The base, $C_9H_{16}N_2$, which Otto and Voigt obtained in addition to triethylic cyanuride, is a reduction product of the latter, from which it is formed by the addition of 1 atom of hydrogen, accompanied by the loss of 1 atom of nitrogen in the form of ammonia. The base, therefore, probably has the constitution $\begin{matrix}CEt{:}N\\|\\CEt{:}N\end{matrix}>CHEt$, the relation between it and triethylic cyanuride being similar to that between cyanophenin and lophine (Radziszewski, Abstr., 1882, 1063). The *aurochloride* of the base forms lustrous, golden needles, and melts at 162—165°. The *picrate* melts at about 130°. The base gives many of the characteristic reactions of the alkaloïds. It combines with silver nitrate to form a double compound, $2C_9H_{16}N_2{,}AgNO_3$, which melts at 122°. When this is again treated with silver nitrate, a second double compound, $2C_9H_{16}N_2{,}3AgNO_3$, is formed.

A. H.

Influence of Configuration on the Action of Enzymes. By E. Fischer (*Ber.*, 1894, **27**, 3479—3483).—The extract prepared by digesting pure, fresh, Frohberg yeast for 20 hours with water

(5 parts) at 35° has no appreciable influence on maltose or on α-methylglucoside. The liquid contains but little matter which is precipitable by alcohol or by boiling; it is, nevertheless, capable of inverting 10 per cent. of its weight of saccharose in 24 hours. Whether the extraction of invertase from very active yeast fails, under these conditions, as observed by O'Sullivan (Trans., 1892, 593) in the case of English high-fermentation yeast, has not been ascertained. When the same yeast (Frohberg type) is ground with powdered glass, the aqueous extract then also hydrolyses maltose and α-methylglucoside, but the action is very feeble, for only 15 per cent. of the glucoside was found to be hydrolysed by 10 parts of the extract in 20 hours at 35°. If, however, a mixture of α-methylglucoside (2 parts), water (20 parts), fresh Frohberg yeast (1 part), and chloroform (1 part) is kept at 35° for three days, fermentation does not occur, but 40 per cent. of the glucoside is hydrolysed. The same result was obtained with maltose.

It is known that water extracts invertase from dried yeast much more readily than from fresh yeast; this also applies to the maltose enzyme. The yeast is allowed to remain in a thin layer, at the temperature of the room, for some days, until it can be pulverised; in this condition it may be kept for a long time. The dried and pulverised yeast is digested with 20 parts of water at 30—35° for 20 hours, and the extract filtered; for this purpose, a Pukall's clay filter may be used. It was with such an enzyme solution that the former experiments (this vol., i, 6) were made, as also those to be described. The precipitation of the maltose enzyme from this solution is much more difficult than that of invertase. If double the volume of alcohol is added, a flocculent precipitate is formed, which, when quickly filtered and dried on a tile in a vacuum, is found to represent 0·5—1 per cent. of the liquid. The solution of this substance in water (25 parts) hydrolyses maltose and α-methylglucoside, but the hydrolytic power is reduced by 4 per cent. as compared with the original solution.

There is a possibility that a single enzyme might have the power, in virtue of the presence of two different atomic groupings within its molecule, of hydrolysing both saccharose and maltose, and that the latter function might be arrested by the action of alcohol (compare Röhmann, this vol., i, 52). The circumstance that by extracting the fresh yeast with water, in which case no arrest of hydrolytic function is conceivable, the saccharose enzyme (invertase) alone is extracted, favours the view that two enzymes are contained in yeast. As to the nature of the second enzyme, little can be said; Röhmann's view, that it is identical with Geduld's glucase (from maize), is misleading, and is also opposed to the fact that the latter observer purified his enzyme by repeated precipitation with alcohol. It bears a closer resemblance to Röhmann's maltose-hydrolysing enzyme from blood, but the identity of the two must remain an open question. The author considers it probable that a large number of maltose-hydrolysing enzymes exist, as there are likewise many enzymes of the type of diastase, and, in order to prevent confusion, it is well to indicate the origin of the enzymes by a prefix, as, for example, yeast-glucase.

Besides Frohberg yeast, the author finds that yeast of the Saaz

type, as well as high-fermentation yeast—the so-called distillery yeast—contains a maltose-hydrolysing enzyme.

Neither fresh nor air-dried milk-sugar yeast gives, on extraction with water at 30°, a solution capable of hydrolysing milk sugar. If, however, the air-dried yeast is carefully ground with powdered glass, and extracted, the liquid obtained hydrolyses milk sugar to the extent of about one-half, and the hexoses formed may be isolated as osazones. The extract of this yeast thus falls short in hydrolytic power, in comparison with that of Kephir grains (Abstr., 1895, i, 7).

Having thus proved the existence of a lactase, the author concludes that, in the fermentation of milk sugar, and, indeed, of every polysaccharide, conversion into simple sugars precedes fermentation. The hydrolysis to simple sugars will generally occur within the yeast cells, as the specific enzymes are retained by the living individuals. Milk-sugar yeast also contains an enzyme which hydrolyses saccharose.

Kephir-lactase and the lactase from milk-sugar yeast hydrolyse neither methylgalactoside nor β-methylglucoside, and no benzaldehyde is formed by their action on amygdalin.

Beer yeast-glucase does not act on methylmannoside (from *d*-mannose), nor on methylsorboside. Methylfructoside (from *d*-fructose, the configuration of which is similar to ordinary glucose) is, however, readily hydrolysed; but invertase is without action on it. α- and β-Methyl-*l*-glucosides are not attacked by beer yeast-glucase.

Emulsin does not act on methyl-*d*-mannoside, methylsorboside, α- and β-methyl-*l*-glucosides, or methylgalactoside. The same applies to lactobionic acid and its calcium salt, although the similarity of this acid to milk sugar would have suggested the contrary.

Myrosin hydrolyses neither α- nor β-methyl-*d*-glucoside.

A. R. L.

Decomposition of Glucose by Alkalis. By F. Gaud (*Compt. rend.*, 1894, **119**, 604—606).—The method described by Causse of limiting the oxidising action of nitric acid on glycerol, by adding a metallic oxide which will form an insoluble salt with the acid produced, is capable of general application, and has been applied by the author to the investigation of the action of alkalis on glucose.

When glucose is treated with alkaline cupric oxide, the greater part is oxidised to tartronic acid, together with small quantities of formic and oxalic acids, but a small portion of the glucose is, at the same time, attacked by the alkali alone, with production of lactic and oxalic acids, phenols, two isomerides of dihydroxyphenylpropionic acid, and, when the glucose is in excess, melassic and glucic acids, constituting the greater part of the resinous products.

The first action of the alkali on glucose produces glucic acid by simple dehydration, but this acid splits up completely into catechol and gluconic acid, the latter in its turn yielding lactic and glyceric acids, whilst the glyceric acid, in presence of the alkali, is converted into lactic and oxalic acids. Interaction between the lactic acid and catechol produces the two isomerides, $OH\cdot C_6H_4\cdot O\cdot CHMe\cdot COOH$ and $OH\cdot C_6H_4\cdot COO\cdot CH\cdot Me(OH)$. Only the hydroxyphenyl acids,

oxalic acid, and lactic acid and its ethereal salts remain when the action is complete. In order to isolate the intermediate products, the employment of various metallic oxides is necessary, the action being then limited to the formation of the particular acid. It is essential that the copper oxide should remain in solution, and this is secured by adding a small quantity of ammonia, which has no effect on the action of the other alkali. Lead hydroxide precipitates glucic and gluconic acids; cadmium hydroxide also precipitates gluconic acid; stannous chloride precipitates lactic acid, bismuth hydroxide, glyceric acid. C. H. B.

Action of Phloroglucinol on Sugars. By C. Councler (*Ber.*, 1895, **28**, 24—28).—Hydrogen chloride was passed into a cooled aqueous solution containing phloroglucinol (1 mol.) and a hexose or pentose (1 mol.). The product, precipitated with water in the case of the hexoses, in the case of the pentoses with alcohol, was dried on a porous plate, and finally washed with alcohol, or dissolved in alcohol and precipitated, and then washed with ether. The substances thus obtained were yellow, red, or green, the colour depending partly on the state of subdivision; they are only slightly soluble in water. They may be regarded as formed from 3 mols. of phloroglucinol and 3 mols. of the sugar with elimination of water; the number of water molecules eliminated is then, in the case of arabinose and xylose, 6; galactose and mannose, 8; dextrose, 9; and levulose, 10. C. F. B.

Two Remarkable Decomposition Products of Saccharose. By E. O. v. Lippmann (*Ber.*, 1894, **27**, 3408—3409).—A disused conduit, formerly employed for "claire," was taken to pieces, when the inner portions of the tubes were found to be incrusted with a thick, black, tasteless, and odourless deposit, having all the properties of the so-called humous matter. This substance had apparently been formed by gradual deposition from the pure sugar solution (claire) remaining in the tubes at a temperature of 35—40°. Alcohol extracted a crystalline substance from the mass, which, after repeated recrystallisation from that solvent, fractional precipitation with basic lead acetate, and treatment with animal charcoal, was separable into mellitic acid and pyromellitic acid. A. R. L.

Maltol. By H. Kiliani (*Ber.*, 1895, **28**, 34; compare this vol., i, 80).—Maltol is obtained in monosymmetric crystals; $a : b : c = 0{\cdot}5902 : 1 : 0{\cdot}3996$. $\beta = 70° 33' 40''$. M. O. F

Methylenitan and Formose. By O. Loew (*Pflüger's Archiv*, 1894, **59**, 276—278).—It is pointed out that Araki (Abstr., 1894, ii, 388) has fallen into error in supposing that Butlerow's methylenitan is the same thing as Loew's formose; the former contains 4 per cent. more carbon than the latter. There is also a question of priority with E. Fischer in regard to the description of the properties of formose. Loew was the first to recognise the formation of true sugars from formaldehyde by condensation. W. D. H.

β-Lævulin. By E. SCHULZE and S. FRANKFURT (*Ber.*, 1894, **27**, 3525—3527).—The crystalline lævulin obtained from unripe rye (Abstr., 1894, ii, 155) has now been prepared in larger quantity. The product obtained differed in many respects from that previously described, which was apparently contaminated with saccharose. β-Lævulin is not converted into glucose by invertase as previously stated; it is lævorotatory, the specific rotatory power in 10 per cent. aqueous solution being $[\alpha]_D = -28{\cdot}6$ to $-28{\cdot}9$. It is very soluble in water, and alcohol precipitates it from the concentrated aqueous solution in the form of minute prisms. The elementary analysis of the substance dried at 100° agrees better with the formula $C_{18}H_{32}O_{16}$ than with $C_{12}H_{22}O_{11}$. On hydrolysis with dilute sulphuric acid, levulose is formed. The authors propose the name *secalose* instead of β-lævulin.

A. R. L.

Steeping ("Quellung") of Starch. By H. RODEWALD (*Landw. Versuchs. Stat.*, 1894, **45**, 201—227).—Dry starch, when placed under cold water or exposed to aqueous vapour, combines with a certain amount of water, and increases slightly in specific gravity. Flückiger showed that starches from different sources have different specific gravities (*Zeit. anal. Chem.*, **5**, 305; compare also Dietrich, *ibid.*, **5**, 51, and Kopp, *Annalen*, **35**, 38). In the present experiments, starch of one kind (wheat) was employed; it was purified by levigation, the water being removed by alcohol and the alcohol by ether. Two products (A and B) were obtained. The specific gravity was determined in air by means of a special volumeter (described with sketch), also under chloroform and under ether. The average of 12 specific gravity determinations (in air) was found to be, for A, 1·5072, of these determinations for B, 1·490. In the remaining experiments, A alone was employed. The following constants were obtained.

Sp. gr. of steeped starch.....	1·6122
Sp. vol. of dry starch.....	0·6635
Sp. vol. of steeped starch	0·6203
Amount of water taken up in steeping.....	0·326
Sp. heat of dry starch.....	14·2 ± 0·234 cal.
Sp. heat of steeped starch.....	0·3728 ± 0·008974
Steeping heat.....	23·4 cal.

It is difficult to ascertain the experimental error in determining the steeping heat; the result is probably low; pressure has no great influence on the steeping heat. The effect of temperature on the steeping heat and on the amount of water absorbed is also discussed. As regards the relations between pressure and decrease of volume in steeping, it is calculated that the shrinking of 1 gram of starch is equivalent to a pressure of 2523 atmospheres. If the shrinking (0·0432 c.c.) is assumed to take place in the 0·326 gram of water absorbed, the shrinkage for 1 gram of water would be 0·1325 c.c. This number, divided by the compression-coefficient of water (0·00004695; compare Wüllner's, *Lehrb. d. Exper.-physik.*, **1**, 275), gives 2821 atmos.

The amount of force developed by starch in steeping is measured by multiplying the decrease of volume per gram (0·0432 c.c.) by the

pressure, as calculated above (2605 kilos.); the maximum amount of force developed by 1 gram of starch in absorbing the greatest amount of water is 1·125 kilos. 11·33 per cent. of the steeping heat may be converted into work. N. H. J. M.

Carbohydrates of Yeast. By E. Salkowski (*Ber.*, 1894, **27**, 3325—3329).—In the preparation of yeast gum (Abstr., 1894, i, 222) by boiling pressed yeast with 3 per cent. aqueous potassium hydroxide, a residue is obtained, which, after it has been treated successively with water, dilute hydrochloric acid, again with water, alcohol, and ether, and finally extracted with ether in a Soxhlet's apparatus to remove fat, consists of an impure cellulose. If the yellowish powder thus obtained is heated in a digester with a large quantity of water under a pressure of 2—2·5 atmcs. for 20 hours, about half is dissolved. The solution gives an intense, brownish-red, iodine reaction, whereas the residue does not give any coloration with iodine. These two substances are accordingly denoted by the author *A-* and *B-cellulose*, or *erythrocellulose*, and *achroocellulose* respectively. When the solution is evaporated to one-fifth, almost the whole of the achroocellulose separates as a jelly, and if the filtrate is mixed with absolute alcohol, the precipitate dehydrated with alcohol and ether, and heated at 110—120°, erythrocellulose is obtained, and may be purified by again extracting with water and repeating the operations just described. It dissolves in water with a slight opalescence, and has a specific rotatory power of $[\alpha]_D = +173·7°$. Analyses point to the formula $C_6H_{10}O_5$, but the substance seems to contain some combined water. On treatment with dilute acids, glucose is formed; saliva also saccharifies it, although the latter acts somewhat more slowly than it does on glycogen. In many points it resembles glycogen, but the opalescence of its solution is less, and would even seem to be due to traces of impurity. The views of Errera (Abstr., 1885, 1151) and of Laurent (*Annal. de l'Institut Pasteur*, 1889, **3**, 113), that glycogen is present in yeast are, in the author's opinion, without sufficient foundation. The author has already observed that the aqueous extract of yeast contains the carbohydrate giving the iodine reaction, and it seems not improbable that this exists in the yeast cells in the dissolved form; the erythrocellulose may be a carbohydrate from which cellulose is formed, or it may be a transformation product of the latter. Cremer has recently stated (*Med. Wochensch.*, 1894, No. 26) that yeast glycogen can be prepared from yeast by Brücke's method (using potassium mercuric iodide), but the author has failed to confirm this observation.

The achroocellulose mentioned above was obtained as a jelly-like mass, which remained unaltered when treated with alcohol. If dried in the water bath, a horny mass was left which could only be pulverised with difficulty. The substance seems not to be homogeneous, for on treatment with acids it yields both glucose and mannose.

A. R. L.

Chitin and Cellulose. By F. Hoppe-Seyler (*Ber.*, 1894, **27**, 3329—3331).—Referring to Winterstein's paper (this vol., i, 80), the author states that he has been engaged for some years in an investigation of the cellulose-like carbohydrates from plants and animals.

Tunicin, from the Tunicata, when heated with potassium hydroxide at 180°, behaves as ordinary cellulose, but chitin from articulated animals (the shells of crabs, scorpions, and spiders were examined), when so treated, although it undergoes no alteration as far as its texture is concerned, is found, after being washed free from alkali, to be readily soluble in dilute acetic acid, forming a solution from which alkali throws down a flocculent precipitate. The percentage of nitrogen in the chitin remains unaltered after this treatment, but from the alkali with which the chitin had been fused, acetic acid was isolated. The author proposes the name *chitosan* for the transformation product of chitin, soluble in acetic acid; it has basic properties, and the *hydrochloride* forms quadratic crystals, soluble in water. When chitosan is treated with concentrated hydrochloric acid it, like chitin, yields glucosamine. If heated with acetic anhydride, it yields a substance resembling chitin, which, when heated with potash at 180°, is resolved into chitosan and acetic acid. Chitosan and propionic anhydride also yield a substance resembling chitin.

Cellulose, when fused with potassium hydroxide at 180°, remains intact, but at 200° it undergoes decomposition. A. R. L.

Decomposition of Chitin. By F. Hoppe-Seyler (*Ber.*, 1895, **28**, 82).—The conversion of chitin into chitosan and acetic acid by fusion with potash, and the formation of acetic acid and glucosamine by the action of hydrochloric acid on chitosan, are in complete accord with Schmiedeberg's view of the constitution of chitin. Chitosan easily combines with various substances, and is usually readily regenerated by the action of alkalis. The products of the interaction of acetic anhydride and chitosan are quite different from those yielded by chitin under similar circumstances, and will be described later. J. B. T.

Production of Gaseous Formaldehyde for Disinfecting Purposes. By R. Cambier and A. Brochet (*Compt. rend.*, 1894, **119**, 607—609).—Trioxymethylene is very easily obtained by mixing the commercial 40 per cent. solution of formaldehyde with about one-fourth its volume of sulphuric acid. When heated alone, trioxymethylene readily volatilises, but condenses entirely as trioxymethylene. In presence of air, however, the formaldehyde remains as such in a proportion which increases with the quantity of air present. Twenty litres of air, into which a few centigrammes of trioxymethylene has been volatilised, remains antiseptic even after eight days. The volatilisation of trioxymethylene from hot plates heated at 200° is not very satisfactory, because admixture with air takes place slowly. The authors have, therefore, employed Hofmann's reaction for the production of gaseous formaldehyde, the apparatus consisting of a reservoir and a burner. The burner consists of a block of asbestos containing a metallic tube, pierced in its upper part with a number of holes, and covered with a large D of platinum gauze. The supply of oxygen is controlled by a regulator similar to that of a Bunsen burner; this regulator is surmounted by a plate of mica forming a chimney. C. H. B.

Valeraldehyde. By L. Bouveault and L. Rousset (*Bull. Soc. Chim.*, 1894, [3], **11**, 300—302).—The ordinary method of oxidising amylic alcohol to valeraldehyde, by allowing it to flow into hot chromic acid mixture, gives a very poor yield, the major part of the product consisting of isobutaldehyde and acetone, from which it is difficult to separate the valeraldehyde. The authors prefer to add the oxidising mixture to the alcohol, thus avoiding the exposure of the newly-formed aldehyde to the risk of further oxidation. The alcohol (1000 grams) is heated on the water bath in a two-necked flask, through one neck of which the oxidising mixture (sodium dichromate 1100, sulphuric acid 900, water 2250 grams) is allowed to flow, whilst the aldehyde vapour passes off through the other. The oily distillate is separated from the accompanying water, dried over fused sodium acetate, and the aldehyde distilled from unchanged alcohol. The yield is 60 per cent. on the alcohol employed. The last traces of water can be removed by means of acetic anhydride, a desiccating agent which the authors have used with advantage in drying other aldehydes, as well as ketones and a terpene. A further quantity of unchanged amylic alcohol can be recovered from the residue in the flask, in which amylic valerate and a resinous substance are also formed during the oxidation. Jn. W.

Action of Sulphur Chloride on the Copper Derivatives of Acetylacetone and Benzoylacetone. By V. Vaillant (*Compt. rend.*, 1894, **119**, 647—650).—When the copper derivative of acetylacetone is dissolved in chloroform, and a solution of sulphur chloride in chloroform is added drop by drop until the blue colour of the liquid disappears, cuprous chloride and sulphur are precipitated, and the liquid, on evaporation, yields a compound, $C_{10}H_{14}S_2O_4$, which crystallises readily in beautiful, rhombic crystals, highly refractive and of an amber-yellow colour, with the faces g_1, h_1, *me*, and $e^{0}/_{2}$. It is quite insoluble in cold water, but dissolves slightly in boiling water, and is only slightly soluble in alcohol, but dissolves readily in ether, benzene, and especially chloroform. It melts at 90—91°, and readily remains in superfusion; when heated in presence of air, it decomposes without boiling. Fuming nitric acid attacks it with almost explosive energy, and potassium permanganate, in presence of light petroleum, yields a crystalline compound which has not yet been analysed.

The sodium derivative, $C_{10}H_{12}Na_2S_2O_4$, is obtained by the action of sodium on a solution in dry ether; it crystallises with difficulty, and dissolves in water, but is decomposed on boiling. The copper derivative is obtained by the action of copper acetate on the sodium compound, or on an ethereal solution of the substance itself; it crystallises, with some difficulty, from chloroform in small, dark green octahedra. When dried at 60°, it has the composition

$$C_{10}H_{12}CuS_2O_4 + 4H_2O,$$

and at 100°, it decomposes.

It will be observed that since the product is a dithio-derivative, the action of sulphur chloride on acetylacetone is not analogous to

its action on ethylic acetoacetate. The dithio-derivative has already been obtained by C. and A. Combes by the action of sulphur chloride on acetylacetone.

The copper derivative of benzoylacetone, when treated with sulphur chloride, yields dithiobenzoylacetone, which crystallises in the rhombic system; it forms a copper compound, and gives a red coloration with ferric chloride. C. H. B.

Action of Methylic Bromopropionate on Sodium Nitrite. By G. Lepercq (*Bull. Soc. Chim.*, 1894, [3], **11**, 297—300).—*Methylic α-bromopropionate* is prepared in the same way as the ethylic salt (Abstr., 1893, i, 65), namely, by heating propionic acid with bromine and sulphur, and subsequently heating the crude bromopropionic acid thus formed with methylic alcohol and concentrated sulphuric acid. The yield of crude product is 91 per cent., and, on fractionation, more than half this quantity is obtained as a colourless liquid boiling at 145—150°, and having a sp. gr. of 1·5 at 15°.

When methylic α-bromopropionate is gently heated with methylic alcohol (1 vol.) and sodium nitrite (2 mols.) (compare Abstr., 1894, i, 114), a deep red colour is gradually developed, and carbonic anhydride, nitrogen, and nitric oxide are evolved. The portion of the product insoluble in water consists of a heavy, yellowish oil, which solidifies on agitation, and, on recrystallisation from methylic alcohol, forms a brilliant, white saccharoidal mass of clinorhombic prisms; it melts at 64°, and then remains in a state of superfusion. Its composition corresponds with that of *methylic dinitrosolactate*, $[COOMe{\cdot}C(NO)Me]_2O$, and it is accordingly hydrolysed by baryta water into acetic acid, hydroxylamine, and carbonic anhydride. The soluble portion of the product contains a small quantity of *methylic α-nitrosopropionate*, which crystallises in small, silky needles from the ethereal extract, and melts at 69°. The *silver* salt forms a white precipitate, and is anhydrous. Sodium ethylnitrolate and sodium acetate also appear to be present.

The author considers that the immediate product of the action between the bromopropionate and the nitrite is methylic α-nitropropionate, and that the substances mentioned above are formed from this by secondary changes. Part condenses to the dinitrosodilactate, and another part is converted into the nitrosopropionate, but the bulk is decomposed by the excess of sodium nitrite into carbonic anhydride and sodium nitrolate; the formation of the latter accounts for the development of the red colour. The nitrolate is in turn decomposed to some extent into sodium acetate and a mixture of nitrogen and nitric oxide, which, with the carbonic anhydride just mentioned, constitute the gases evolved. Jn. W.

Ethylic Nitrosopropionate. By G. Lepercq (*Bull. Soc. Chim.*, 1894, [3], **11**, 295—296; compare Abstr., 1894, i, 114).—An improved method of preparation. A mixture of alcoholic ethylic α-bromopropionate (100 grams in 300 grams of alcohol) and aqueous sodium nitrite (100 grams in 100 grams of water) is homogeneous. At the ordinary temperature, however, and in the course of 10 days, complete

interaction takes place, and, after the solvents have been allowed to evaporate from an open vessel in the cold, a large yield of crude ethylic nitrosopropionate (62 per cent.) may be extracted with ether from the residue; on recrystallisation from alcohol, the nitrosopropionate is obtained in long, light, brilliantly white needles. The method is applicable to the butyrates and valerate. Jn. W.

Diamido-ethers. By R. Anschütz and K. Stiepel (*Ber.*, 1895, **28**, 60—62).—Representatives of the class of diamido-ethers, of the general formula $R{\cdot}C(NH_2)_2{\cdot}OR'$, have not hitherto been prepared.

Methylic dianilido-oxalate (methylic dianilidomethoxyacetate), $COOMe{\cdot}C(NHPh)_2{\cdot}OMe$, is obtained by acting with dry aniline on methylic dichloroxalate (methylic dichloromethoxyacetate), $COOMe{\cdot}CCl_2{\cdot}OMe$, in dry ethereal solution. It is a viscid liquid, which decomposes when heated. It combines with 2 mols. of hydrogen chloride to form a solid *hydrochloride*, and it also yields a *platinochloride*.

Methylic semiphenylimido-oxalate (methylic phenylimidomethoxyacetate), $COOMe{\cdot}C(OMe){:}NPh$, is produced when the foregoing action is carried out in boiling xylene solution, and forms crystals melting at 111°. When ammonia is passed into an ethereal solution of this substance, *methylic amidoanilido-oxalate* (methylic amidoanilidomethoxyacetate), $COOMe{\cdot}C(NH_2)(NHPh){\cdot}OMe$, is formed as a white powder which melts at 215°. The corresponding *diparatoluido*-compound melts at 105°, whilst the *dipiperido*-compound boils at 166° under a pressure of 20 mm. without undergoing decomposition.

Methylic semiortho-oxamate, $CONH_2{\cdot}C(OMe)_3$, which melts at 118°, is obtained by heating methylic semiphenylimido-oxalate (methylic phenylimidomethoxyacetate) with ammonia dissolved in methylic alcohol.

Diphenylamidinoxalanilide, $NHPh{\cdot}CO{\cdot}C(NHPh){:}NPh$, which is found among the products of the action of aniline on methylic dichloroxalate (methylic dichloromethoxyacetate), has previously been described by Klinger (this Journ., 1877, i, 710), who gives the melting point as 234—235° instead of 134—135°.

Diparatolylamidinoxaloparatoluidide,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(NHC_7H_7){:}NC_7H_7,$$

melts at 182°.

Semiorthoxalopiperidide, $NC_5H_{10}{\cdot}CO{\cdot}C(C_5NH_{10})_3 + 3MeOH$, is a liquid, the constitution of which cannot as yet be regarded as proved. A. H.

Glyoxylic acid. By C. Boettinger (*Arch. Pharm.*, 1894, **232**, 549—557; compare Abstr., 1894, i, 402).—According to the author, glyoxylic acid cannot be crystallised, as the syrupy solution decomposes on further concentration; the minute bubbles of carbonic anhydride gave it, however, the appearance of a solid.

A gelatinous modification of the calcium salt is obtained by evaporating its solution and allowing it to cool. This jelly effloresces, especially in direct sunlight, and ultimately is suddenly transformed into a mixture of fine crystals and clear dilute solution.

The acid interacts with hydrazine sulphate to form an intensely red substance; in hot solutions, however, this is decomposed, and carbonic anhydride and ammonia are liberated. Ammonia decomposes glyoxylic acid in a similar manner.

A colourless, viscid liquid of spirituous odour, probably an *acetal*, results from the action of glyoxylic acid on alcohol in the presence of sulphuric acid in the cold, but is decomposed by heat into formaldehyde and other products. It is soluble in water, and forms a white, insoluble *calcium salt*.

A paste of glyoxylic acid and thiocarbamide acquires a bright scarlet colour, due to a substance containing sulphur and nitrogen. This is insoluble in alcohol, but freely soluble in alkalis forming a solution of the same colour, from which coloured compounds are precipitated by metallic salts. It cannot be obtained from formaldehyde or dichloracetic acid; the latter forms a white product with thiocarbamide, which is only sparingly soluble in alkalis.

Bisdimethylamidophenylacetic acid, $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}COOH$, crystallises in colourless needles from a solution of dimethylaniline and glyoxylic acid in the minimum quantity of alcohol. It melts at 171°, and is sparingly soluble in boiling water, readily in alkalis. The acid is dissolved by concentrated sulphuric and acetic acids. It is readily oxidised by air, mercuric chloride, &c., to a substance of intense blue colour, but is decomposed by bromine, parabromodimethylaniline being formed. The *ethylic* salt crystallises in slender, colourless needles, and melts at 68°.

α-Naphthylamine condenses with glyoxylic acid in alcoholic solution to form a bright brown powder, $C_{12}H_9NO_2$, which is soluble in ammonia, but insoluble in alcohol and dilute acids. The *barium* salt is reddish-brown.

Similar products result from the condensation of orthotoluidine and metaphenylenediamine with glyoxylic acid; the first is intensely yellow, the second a black powder. Glyoxylic acid also condenses with resorcinol and catechol, but not with quinol or dimethoxyquinol, in the molecules of which the para-positions are occupied.

JN. W.

Action of Ethylic Isosuccinate on Ethylenic Bromide. Constitution of Vinaconic acid. By R. MARBURG (*Ber.*, 1895, **28**, 8—12).—When ethylic sodioisosuccinate, $CMeNa(COOEt)_2$, is treated in alcoholic solution with ethylenic bromide, about 15 per cent. of it is converted into *ethylic γ-bromethylisosuccinate*,

$$CH_2Br{\cdot}CH_2{\cdot}CMe(COOEt)_2.$$

This is a colourless, rather viscous, oil, boiling at 134—135° under 8 mm. pressure; at 200° it decomposes quantitatively into ethylic bromide and *ethylic α-methylbutyrolactonecarboxylate*,

$$\begin{matrix} CH_2{\cdot}CH_2{\cdot}CMe{\cdot}COOEt \\ | \qquad\qquad | \\ O\text{———}CO \end{matrix},$$

which boils at 262—263° under 755 mm. pressure; the *acid* itself crystallises in colourless prisms and melts at 98°, it is obtained by

hydrolysing the bromo-acid with baryta water, and adding acid to the barium salt of γ-hydroxyethylisosuccinic acid,

$$OH\cdot CH_2\cdot CH_2\cdot CMe(COOH)_2,$$

formed; the acid is itself not capable of existence, but at once loses water and forms the lactone-acid.

When, however, ethylic sodiomalonate, in which a hydrogen atom is still attached to the carbon atom, is treated with propylenic bromide, the ethylic salt of a bromo-acid is not formed, but instead the ethylic *salt* of a dibasic acid containing no bromine, *ethylic methylvinaconate* (*trimethylenedicarboxylate*), boiling at 106—107° under 8 mm. pressure. The action is not at all analogous to the preceding one, and hence there can be little doubt that vinaconic acid, which is formed in a similar way by the action of ethylenic bromide on ethylic sodiomalonate, is not vinylmalonic acid, $CH_2{:}CH\cdot CH(COOH)_2$ (Fittig and Rœder, Abstr., 1883, 730), but trimethylenedicarboxylic acid,

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C(COOH)_2,$$

(compare W. H. Perkin, jun., Trans., 1885, 801; 1887, 849).

C. F. B.

Isomeric Osazones of Ethylic Dioxysuccinate. By R. Anschütz and H. Pauly (*Ber.*, 1895, **28**, 64—69).—When ethylic dioxysuccinate is treated with phenylhydrazine a number of different compounds is formed. When the ethereal salt is added to an alcoholic solution of the hydrazine, an additive compound,

$$COOEt\cdot CO\cdot CO\cdot COOEt,2N_2H_3Ph,$$

is obtained, which crystallises in fascicular groups of slender white needles, melting and decomposing at 116—118°. When this is kept, either alone or covered with ether, it is converted into the α-osazone, whereas if covered with alcohol, it passes into the β-osazone. The *monophenylhydrazone* may be prepared by the addition of phenylhydrazine to a well cooled alcoholic solution of the ethereal salt. It melts at 72—73°, and when treated in ethereal solution with sulphurous anhydride or hydrogen chloride passes into a less soluble modification melting at 77°.

Three isomeric ozazones have also been prepared, of which the α-compound has already been described (Abstr., 1891, 725). The three differ from one another in crystalline habit, melting point, and solubility. The α-compound melts at 120—121°, the β-compound at 136—137°, and the γ-compound at 173—175°; the β- and γ-compounds are respectively 10 and 100 times less soluble in ether than the α-compound. The α-modification readily changes into the β-form when iodine or sulphurous anhydride is added to its ethereal solution. Both the α- and γ-forms are changed into the β-form when they are boiled for some time with an indifferent solvent. It has hitherto been found impossible to convert the β-form into either of the others. All three modifications are converted by acetic acid into the same pyrazolone-derivative as was obtained from the α-modification by Anschütz and Parlato (Abstr., 1892, 1181). The α-osazone is converted by

oxidation into the corresponding *osotetrazone*, $\begin{matrix}NPh{\cdot}N{:}C{\cdot}COOEt\\ |\\ NPh{\cdot}N{:}C{\cdot}COOEt\end{matrix}$, which crystallises in slender, violet-black needles, or flat, garnet-red prisms, melting and decomposing at 143°. The β- and γ-modifications do not yield this substance. Propylic dioxysuccinate behaves towards phenylhydrazine in a similar manner to the ethylic salt. An additive compound, melting at 112°, is the first product, and isomeric osazones have been obtained but not yet investigated. They are converted by acetic acid into a pyrazolone derivative melting at 115°.

With phenylhydrazine, the pyrazolone-compounds obtained by heating the osazones of both the propylic and ethylic salts yield a compound, which melts at 256°; its formula is $C_{16}H_{16}N_4O_3$, but its constitution has not yet been ascertained.

The osazone of ethylic ketipate is also converted by acetic acid into a substance which melts and decomposes at 275° and seems to be a bis-pyrazolone derivative of the formula

$$\begin{matrix}NPh{-}N\\ |\\ CO{\cdot}CH_2\end{matrix}\!\!>C{\cdot}C<\!\!\begin{matrix}N{-}NPh\\ |\\ CH_2{\cdot}CO\end{matrix},$$

although it may possibly be a bis-pyridazolone-compound.

A. H.

Disubstituted Alkylic Tartrates. By P. Freundler (*Bull. Soc. Chim.*, 1894, [3], **11**, 305—317).—In order to test the validity of Guye's well-known formula, the rotatory powers of the alkylic salts of various acidyltartaric acids of the type of methylic diacetyltartrate were determined. As these were mostly liquids of uncertain stability at their boiling points, the mode of purification of the product obtained by the action of the alkylic tartrate on the acid chloride at 100° was modified, the ethereal salt being extracted from the washed product with ether, and the latter removed from the dried extract in a dry atmosphere and at a low temperature.

The alkylic diacidyltartrates are heavy, tasteless, neutral solids or liquids, which decompose readily when distilled, even under very low pressures. The boiling points rise, and the densities diminish, as the series is ascended. Cryoscopic observations in benzene and ethylenic bromide show that the molecules are simple. The rotatory powers, whether of the liquids or of their alcoholic solutions, are practically independent of the temperature. The diacidyltartrates are completely hydrolysed by alkalis or sodium ethoxide, and partially and slowly by water; they are resolved by alcoholic ammonia, at a high temperature, into the alcohols, the fatty amides, and tartramide, the latter undergoing further hydrolysis into tartramic acid. They are decomposed by phosphoric pentachloride into the fatty acid chlorides, and the alkylic chlorotartrates, but the latter decompose further, especially at high temperatures, into hydrogen chloride and the corresponding chlorofumarates.

Methylic diacetyltartrate crystallises in rhomboidal, oblique prisms, melts at 103°, and boils at 182—183° (21 mm.). The rotatory power in alcoholic solution is $[\alpha]_D = -15{\cdot}5°$. The *ethylic* salt crystallises in clinorhombic prisms, melts at 66·5°, and boils at 190—192°

(21 mm.), and at 291° under atmospheric pressure. The rotatory power of the superfused substance is $\alpha = +5°$ for 100 mm.; of the alcoholic solution, $[\alpha]_D = +0·3°$. The *propylic* salt melts at 31°, and boils at 195—197° (13 mm.), at 204° (16 mm.), at 216° (70 mm.), at 233—235° (100 mm.), and at 313° under atmospheric pressure. The rotatory power of the superfused substance is $\alpha = 13·4°$ for 100 mm.; of the alcoholic solution, $[\alpha]_D = +7·0°$. *Butylic tartrate* crystallises in elongated prisms, melts at 21—22°, and boils at 208° (12 mm.); sp. gr. = 1·098 at 22°. The rotatory power of the superfused substance is $[\alpha]_D = +10·3°$; of the alcoholic solution, $[\alpha]_D = +11·3°$. *Butylic diacetyltartrate* boils at 214° (20 mm.), and at 218° (23 mm.); sp. gr. = 1·096 at 15·5°. The rotatory power of the liquid at 20°, $[\alpha]_D = +8·0°$; of the alcoholic solution at 22°, $[\alpha]_D = +8·8°$.

Methylic dipropionyltartrate crystallises in large prisms. It melts at 27—27·5°, and boils at 184—185° (12 mm.), at 189—190° (15 mm.), and at 287—289° (730 mm.); sp. gr. = 1·181 at 15°. The rotatory power of the superfused substance at 15°, $[\alpha]_D = -10·7°$; of the alcoholic solution at 20°, $[\alpha]_D = -12·4°$. The *ethylic* salt boils at 202° (16 mm.), and can be distilled, with but little decomposition, under atmospheric pressure; sp. gr. = 1·124 at 14°. The rotatory power of the liquid at 23°, $[\alpha]_D = +0·4°$; of the alcoholic solution, $[\alpha]_D = +1·2°$. The *propylic* salt boils at 207° (15 mm.), and at 222—225° (45 mm.); sp. gr. = 1·018 at 15°. The rotatory power of the liquid at 16°, $[\alpha]_D = +5·6°$; of the alcoholic solution, $[\alpha]_D = +6·3°$. The *butylic* salt boils at 212° (12 mm.), at 216° (20 mm.), and at 230—231° (36 mm.); sp. gr. = 1·068 at 15·5°. The rotatory power of the liquid at 12°, $[\alpha]_D = +6·9°$; of the alcoholic solution, $[\alpha]_D = +8·0$.

Methylic dibutyryltartrate boils at 200—203° (11 mm.), at 212° (26 mm.), and at 300—302° (731 mm.); sp. gr. = 1·145 at 14°. The rotatory power of the liquid at 13°, $[\alpha]_D = -15·1°$; of the alcoholic solution, $[\alpha]_D = -12·6°$. The *ethylic* salt boils at 212—215° (24 mm.); sp. gr. = 1·105 at 15·5°. The rotatory power of the liquid at 16°, $[\alpha]_D = -0·8°$; of the alcoholic solution, $[\alpha]_D = +0·3°$. The *propylic* salt boils at 208—211° (17 mm.), at 221—222° (28 mm.), and at 226—227° (40 mm.); sp. gr. = 1·067 at 15·5°. The rotatory power of the liquid at 13°, $[\alpha]_D = +5·2°$; of the alcoholic solution, $[\alpha]_D = +7·2°$.

The divaleryltartrates were prepared by means of *normal valeric chloride*. This is a liquid which boils at 127—128°, and has sp. gr. = 1·0155 at 15°. *Methylic divaleryltartrate* boils at 208—210° (11 mm.); sp. gr. = 1·101 at 18°. The rotatory power of the liquid at 15°, $[\alpha]_D = -16·1°$; of the alcoholic solution, $[\alpha]_D = -12·9°$. The *ethylic* salt boils at 214—215° (11 mm.); sp. gr. = 1·068 at 12°. The rotatory power of the liquid at 15°, $[\alpha]_D = 2·0°$; of the alcoholic solution, $[\alpha]_D = -0·7°$. The *propylic* salt boils at 223° (12 mm.); sp. gr. = 1·050 at 16·5°. The rotatory power of the liquid at 17°, $[\alpha]_D = +3·3°$; of the alcoholic solution, $[\alpha]_D = +3·6°$. The *butylic* salt boils at 229—230° (13 mm.), at 243° (28 mm.), at 269—270° (60 mm.), and at 340—350° under atmospheric pressure; sp. gr. = 1·031 at 13°. The rotatory power of the liquid at 15°, $[\alpha]_D = +4·8°$; of the alcoholic solution, $[\alpha]_D = +6·0°$.

Methylic dicaproyltartrate has a sp. gr. = 1·078 at 14°. The rotatory power of the liquid at 16° is $[\alpha]_D = -15·9°$; of the alcoholic solution, $[\alpha]_D = -12·4°$. The *ethylic* salt has a sp. gr. = 1·049 at 14·5°. The rotatory power of the liquid at 16° is $[\alpha]_D = +3·1°$; of the alcoholic solution, $[\alpha]_D = +1·1°$. The *propylic* salt boils at 242—243° (40 mm.); sp. gr. = 1·027 at 15°. The rotatory power of the liquid at 16°, $[\alpha]_D = -2·2°$; of the alcoholic solution, $[\alpha]_D = -3·6°$.

The rotatory powers of these alkylic acidyltartrates vary in general in the same sense as Guye's product of asymmetry, the introduction of positive radicles causing a positive increase or negative decrease in both, and that of negative radicles having the opposite effect. But there are certain modifications necessary, for the addition of a $-CH_2$ group has a greater effect when the radicle is alkylic than when it is oxylic, so that the structure of the latter kind must be closer, or more compressed, than that of the former. To allow for the corresponding difference in the moments of the masses of the radicles, the author introduces a fifth quantity, m, into Guye's formula; a multiple of the mass of a $-CH_2$ group. The formula thus becomes

$$P = \frac{m(a-c)(a-d)(a-c-m)(a-d-m)(c-d)}{(2a+b+c+d-m)^6}.$$

The influence of m increases with the length of the chain, but is not always exerted in the same sense, so that the value of P passes in any particular series through several maxima and minima. A corresponding change in sign is to be expected in the rotatory power, and may be observed in several instances; between methylic tartrate and methylic diacetyltartrate, for instance, also in the ethylic series, and in the dibutyryltartrates.

	P.	$[\alpha]_D$.
Methylic dibutyryltartrate	−19·35	−15·1°
Ethylic „	−9·23	−0·8
Propylic „	0	+6·2
Butylic „	+7·0	+6·0

The modified form of Guye's formula is therefore valid qualitatively, even when the substituted chains are of considerable length.

Jn. W.

Sarcosine. By W. Paulmann (*Arch. Pharm.*, 1894, **232**, 601—639).—Sarcosine is best prepared by the hydrolysis of caffeine with baryta, the yield being 60 per cent. of the theoretical; the yield obtained by the action of ethylic chloracetate on methylamine is extremely poor. The free base is conveniently prepared from the hydrochloride by neutralising it with an alkali, and extracting the evaporated residue with alcohol. The *hydrobromide*, *hydriodide*, and other salts are described. There does not seem to be an oxalate, so that the basic properties of sarcosine are less marked than those of glycocine; the same is true of the acid properties, for neither the alkali nor silver salts, nor those of the alkaline earths, nor the alkylic salts could be prepared; the *nickel* and *zinc* salts are described. In preparing

betaïne by the action of methylic iodide on sarcosine, the methylic compound of the latter was obtained; its *platinochloride* is described. The formation of dimethylamine (Abstr., 1884, 994) in the dry distillation of sarcosine, as described by Mylius, was not observed. Nitrososarcosine possesses acid properties stronger than those of the parent substance, as it forms calcium and *silver* as well as *copper* and *nickel* salts; a barium salt, however, could not be prepared; the basic properties are very feeble, as it does not form a platinochloride or an aurochloride. On reducing an acetic acid solution of the calcium salt with zinc dust, a substance having strongly reducing properties is formed.

Sarcosine hydrochloride is converted by a mixture of fuming nitric and fuming sulphuric acids into *nitrosarcosine*, $NO_2 \cdot NMe \cdot CH_2 \cdot COOH$, a yellow, crystalline, hygroscopic powder, melting at 164—168°. This gives the nitrate reaction with ferrous sulphate and sulphuric acid, and a colour-reaction with sulphuric acid and phenol resembling that given by guanidine.

Benzoylsarcosine (methylhippuric acid), NMeBz·CH·COOH, could not be crystallised, owing to its extreme solubility; the *calcium* and *copper* salts are described. *Acetylsarcosine* (methylaceturic acid) crystallises in long, thick needles, and melts at 134—138°; the *copper* and *silver* salts are described. Jn. W.

Paradimethylamidobenzylic Alcohol. By L. Rousset (*Bull. Soc. Chim.*, 1894, [3], **11**, 318—320).—This alcohol was prepared from paradimethylbenzaldehyde, made by projecting the condensation product of dimethylaniline and chloral hydrate in small portions at a time into boiling 30 per cent. caustic soda (compare Knoefler and Boessneck, Abstr., 1888, 267). The aldehyde, which crystallises out on cooling, is pure enough for most experiments; on reduction with sodium amalgam in aqueous alcoholic solution, it does not yield the expected alcohol, but a *substance* melting at 155°, which is under investigation. The alcohol is best prepared by the action of boiling, concentrated, aqueous potash; the portion of the product insoluble in water, but soluble in ether, consists chiefly of the alcohol, whilst the soluble portion consists of the potassium salt of *paradimethylamidobenzoic acid*; this acid melts at 235°. The ethereal solution on fractionation under low pressure yields *paradimethylamidobenzylic alcohol*, which forms white crystals, melts at 62°, and boils at 180—190° (18 mm.); it is turned yellow by light. The *platinochloride* crystallises in yellow needles. The *acetate* forms reddish-white crystals and melts at 102°

Jn. W.

Action of Phosphorus Pentachloride on Succinanil. By R. Anschütz and C. Beavis (*Ber.*, 1895, **28**, 57—58; compare Abstr., 1891, 1047).—In addition to dichloromaleïnanil dichloride, described in their previous paper, the authors have obtained *tetrachloro-1-phenylpyrroline*, C_4NCl_4Ph, by the action of phosphorus pentachloride on succinanil. This compound melts at 93°, and is less soluble in light petroleum than the dichloromaleïnanil chloride.

Dichloromaleïnanil itself, when treated with phosphorus pentachlo-

ride, yields *tetrachlorosuccinanil*, $NPh<\begin{matrix}CO\cdot CCl_2\\ |\\ CO\cdot CCl_2\end{matrix}$, melting at 157°, and also dichloromaleïnanil chloride.

Dichloromaleïnanil reacts with bases when heated with them. Aniline produces *anilidochloromaleïnanil*, $NPh<\begin{matrix}CO\cdot C\cdot NHPh\\ ||\\ CO\cdot CCl\end{matrix}$, melting at 188°, whilst monomethylaniline yields the corresponding *methyl*-derivative, melting at 189°.

Dichloromaleïnanil dichloride also reacts with aniline, *dichloromaleïndianil*, $CCl<\begin{matrix}CCl\cdot C:NPh\\ |\\ CO\cdot NPh\end{matrix}$, which melts at 186°, being formed.

Dichloromaleïn-paratoluildipiperidide, $CCl<\begin{matrix}CCl\cdot C(C_5NH_{10})_2\\ |\\ CO\cdot N\cdot C_6H_4Me\end{matrix}$, separates from acetone in splendid yellow crystals, and melts at 107°. On reduction, dichloromaleïnanil dichloride is converted into *γ-anilidobutyrolactam*, $NPh<\begin{matrix}CH_2\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}$, which melts at 68°.

A more detailed account of these investigations is shortly to be published. A. H.

Constitution of Succinanil. By R. Anschütz (*Ber.*, 1895, **28**, 59—60; compare the foregoing Abstr.).—The formation of tetrachloro-1-phenylpyrroline from succinanil is a strong argument in favour of the symmetrical formula, $NPh<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}$, for the latter substance. The reduction of dichloromaleïnanil dichloride to γ-anilidobutyrolactam also seems to show that dichloromaleïnanil, and therefore also succinanil, are symmetrical. There is thus not a single fact in favour of the asymmetrical formula. A. H.

Paramidoacetophenone and Paramidophenylmethylcarbinol. By L. Rousset (*Bull. Soc. Chim.*, 1894, [3], **11**, 320—322).—Paramidoacetophenone is best prepared by heating acetanilide, acetic anhydride, and zinc chloride in molecular proportions in a reflux apparatus on an oil bath for several hours; the oily product is then poured into water, partially neutralised with caustic soda, and the pasty mass which separates on cooling is dissolved in concentrated hydrochloric acid. The liquid thus obtained is made alkaline with soda, and the aniline, liberated from the unchanged acetanilide, is distilled off with steam; the paramidoacetophenone is separated from the residue partly in the crystalline form, and partly by extraction with ether and alcohol. The purified ethereal solution on fractionation yields the ketone, boiling at 195—210° under 18 mm. pressure, and in quantity amounting to 26 to 30 per cent. of the acetanilide employed (compare Drewsen, Abstr., 1882, 847, and Klinger, Abstr., 1886, 60). Paramidoacetophenone, when reduced with sodium amalgam in aqueous alcoholic solution, yields a *substance* crystallising in white needles and melting at 250°, and an oil which, on purification, yields *paramidophenylmethylcarbinol;* the latter forms white crystals, is

soluble in water and in the usual solvents, and turns yellow on exposure to light. It melts at 93°, and boils under 18 mm. pressure at 190°. The *platinochloride* crystallises in small, yellow needles. The diacetyl-derivative, $NHAc{\cdot}C_6H_4{\cdot}CHMe{\cdot}OAc$, forms white crystals and melts at 192°. JN. W.

Diagnosis of Orthosubstituted Aromatic Acids by means of the Iodoso-reaction. By V. MEYER (*Ber.*, 1895, **28**, 83—84).—It has been shown by the author and his students that orthoiodobenzoic acids are converted into iodoso-derivatives (1) by solution in fuming nitric acid; (2) by boiling with potassium permanganate and sulphuric acid; (3) by the action of an alkali on the iododichlorides. The meta- and para-iodo-acids are nitrated by the first method, not altered or completely oxidised by the second, and regenerate the iodides from the iododichlorides. Willgerodt's preparation of meta- and para-iodoso-acids (Abstr., 1894, i, 590) by other methods in no way invalidates the author's statement that the above reactions afford a ready means of distinguishing orthoiodo-acids from the para- and meta-compounds. The paper concludes with a summary of Grahl's investigation of iodo-isophthalic acid. J. B. T.

Electrolytic Reduction of Paranitrobenzoic acid. By A. A. NOYES and A. A. CLEMENT (*Amer. Chem. J.*, 1894, **16**, 511—513; compare Abstr., 1893, i, 406).—The authors have previously shown that paramidophenolorthosulphonic acid is obtained on electrolysing nitrobenzene in sulphuric acid solution. This behaviour is characteristic of nitro-compounds in general (compare Gattermann, Abstr., 1894, i, 72), the reduction of the nitro-group being accompanied by a migration of one of its oxygen atoms to the para-position. Only those compounds in which the para-position is already occupied by some group or element other than hydrogen form exceptions to this rule. Paranitro-orthotoluidine, for example, gives rise to diamidocresol, $[Me : (NH_2)_2 : OH = 1 : 2 : 4 : 5]$, a migration of oxygen to the ortho-position taking place. Paranitrotoluene similarly yields amidobenzylic alcohol, a substitution of hydroxyl in the methyl group occupying the para-position. On electrolysis of a warm solution of paranitrobenzoic acid (12 grams) in concentrated sulphuric acid (100 grams), by passing a current of 1 ampère for 24 hours, paramidophenolsulphonic acid is formed, the tendency of the oxygen atom to assume the para-position having been sufficient to expel the carboxyl-group originally occupying it. G. T. M.

Preparation of Benzoic Anhydride. By A. DENINGER (*J. pr. Chem.*, 1894, [2], **50**, 479—480).—Although benzoic chloride does not react with dry sodium carbonate, a violent action takes place when pyridine is added to the mixture, the anhydride being formed quantitatively. Picoline or quinoline may be substituted for pyridine, but dimethylaniline does not produce the same effect.

Mercuric oxide, cupric oxide, and litharge all behave in a similar manner to sodium carbonate; zinc oxide acts without the addition of pyridine, whilst barium carbonate and ferric oxide do not produce

the violent action under any circumstances (compare Claisen, this vol., i, 139). A. H.

Bismuth Nitrosalicylates. By H. Causse (*Compt. rend.*, 1894, **119**, 690—699).—Double decomposition between bismuth nitrate and a soluble salicylate is rarely complete, and a reaction gradually takes place in the mother liquor, the result depending on the concentration. Sometimes white, silky needles separate; sometimes the colour of the crystalline precipitate is yellow or orange Even in dilute solutions, the nitric acid of the bismuth nitrate converts the salicylic acid into β-nitrosalicylic acid, which yields normal and basic salts acccrding to the conditions, the energy of the phenolic function being augmented by the introduction of the NO_2 group. The red colour of bismuth salicylate, which is usually attributed to iron, is really due to a nitrosalicylate. *Bismuth β-nitrosalicylate*, $[C_6H_3(NO_2)(OH)\cdot COO]_3Bi + 2H_2O$, is obtained in long, silky needles from the mother liquor from the preparation of bismuth salicylate, and also by dissolving 20 grams of salicylic acid in 100 c.c. of acetic acid and adding 150 c.c. of water and 15 grams of normal bismuth nitrate dissolved in 50 c.c. of a saturated solution of potassium nitrate; an action at once begins, and soon becomes violent if the liquid is not cooled. The nitrosalicylate is decomposed by boiling water into bismuth oxide and nitrosalicylic acid; with ferric chloride it gives an intense red coloration. *Basic bismuth β-nitrosalicylate*, $OH\cdot Bi<\begin{smallmatrix}COO\\ __O\end{smallmatrix}>C_6H_3\cdot NO_2 + H_2O$, is obtained by gently heating a solution of 20 grams of salicylic acid in 100 c.c. of acetic acid with a solution of 30 grams of bismuth nitrate in 300 c.c. of a saturated solution of potassium nitrate. The salt forms small, lemon-yellow needles, with properties similar to those of the normal salt; it is decomposed by water, and gives a red coloration with ferric chloride. A second *basic bismuth nitrosalicylate*, $Bi_2(OH)_2[C_6H_3(NO_2)(OH)\cdot COO]_2 + H_2O$, separates in orange-red, microscopic needles when the liquid from which the preceding compound has separated is very nearly neutralised with sodium carbonate.

β-Nitrosalicylic acid, [COOH : OH : NO_2 = 1 : 2 : 5], is obtained by the action of boiling water on any one of the bismuth nitrosalicylates. It crystallises from water and melts at 227·5°. It gives a blood-red coloration with ferric chloride, and forms a barium salt which crystallises in lemon-yellow lamellæ. C. H. B.

Synthesis of α-Phenyl-β-benzoylpropionic acid. By R. Anschütz and W. Montfort (*Ber.*, 1895, **28**, 63—64).—In order to confirm a previously expressed view as to the formation of mesitonic acid from mesityl oxide (Abstr., 1888, 1272), the authors have effected the synthesis of α-phenyl-β-benzoylpropionic acid from benzylideneacetophenone. The additive compound of this ketone with hydrogen chloride, $CHPhCl\cdot CH_2\cdot COPh$ (Claisen and Claparède, Abstr., 1882, 511), can readily be converted into the *nitrile* which melts at 127°, and the *acid* melting at 153°. α-Phenyl-β-benzoylpropionic acid is converted by reduction into *αγ-diphenylbutyrolactone*,

$CHPh<\begin{matrix}CH_2\cdot CHPh\\ CO\cdot O\end{matrix}$, which melts at 109°. Acetic chloride converts the acid into *αγ-diphenylcrotolactone*, $CHPh<\begin{matrix}CH{:}CHPh\\ CO\cdot O\end{matrix}$, which melts at 103°. The phenylhydrazone is unstable and is readily converted into *triphenylpyridazolone*, $N<\begin{matrix}CPh\cdot CH_2\\ NPh\cdot CO\end{matrix}>CHPh$. Full details of the investigation are to be shortly published. A. H.

Ethylic Dinitroterephthalate: A Correction. By C. Haeusermann and E. Martz (*Ber.*, 1895, **28**, 81—82).—By the action of alcohol and hydrogen chloride on dinitroterephthalic acid, $[(NO_2)_2 = 3 : 5]$, the ethylic hydrogen salt is formed, not the diethylic salt as previously stated (Abstr., 1894, i., 131). The acid therefore follows V. Meyer's rule. The ethylic hydrogen salt readily dissolves in alkalis, is not reddened by excess, and on warming in aqueous solution, decomposes silver carbonate, a soluble silver salt being produced. J. B. T.

Derivatives of Gallic acid. By C. Boettinger (*Arch. Pharm.*, 1894, **232**, 545—549, compare Abstr., 1892, 181, and 1894, i, 13).—The action of a mixture of glycerol and hydrogen potassium sulphate on gallic acid is not analogous to its action on tannin, as, instead of condensation and hydration, reduction and oxidation take place; a similar action occurs in the reduction of dialuric acid to acid ammonium hydrurilate by this mixture.

The products are separated by means of alcohol; the relative yield varying accordingly as the gallic acid is hydrated or anhydrous. The reduction product, *hydrogalalic acid*, $C_{14}H_{16}O_8 + H_2O$, has the same formula as octohydrorufigallic acid, and is peach coloured. It is insoluble in water, but soluble in alcohol, methylic alcohol, aniline, and ammonia; the colour of the ammoniacal solution is at first blue, but soon changes through intense violet to brown. Hydrogalalic acid is almost entirely destroyed by fusion with potash, and yields only a small quantity of a very oxidisable oil, when distilled with zinc dust; this oil does not possess the characteristic odour of the corresponding products from hydrotannic and hydroquercitannic acids. The acid dissolves freely in fuming sulphuric acid. The *acetyl* derivative, $C_{14}H_{14}Ac_2O_8$, crystallises in yellowish-grey plates.

The oxidation *product*, $C_{12}H_{14}O_9 + 2H_2O$, appears to be a derivative of pyrogallol; it is a dull, brownish-violet powder, and is insoluble in water and ammonia, although its colour is changed to violet by the latter. It yields an *acetyl* derivative, $C_{12}H_{13}AcO_9$, a brownish-grey substance insoluble in water, alcohol, and cold dilute soda.

Jn. W.

Stereoisomerism of Diazo-Compounds. By A. Hantzsch (*Ber.*, 1894, **27**, 3527—3547; compare E. Bamberger, this vol., i, 25).—The unstable character of potassium benzenesyndiazosulphonate renders the analyses of little value in determining its composition;

salts of analogous diazo-compounds, however, may be analysed without difficulty, owing to their greater stability.

Potassium parachlorobenzenesyndiazosulphonate, $\begin{matrix}C_6H_4Cl\cdot N\\ \|\\ SO_3K\cdot N\end{matrix} + H_2O$, is obtained in bright red crystals which remain unchanged in air for several hours, but ultimately become discoloured; the *anti*-salt is anhydrous.

Potassium parabromobenzenesyndiazosulphonate also contains $1H_2O$, and becomes discoloured on exposure to air. *Potassium orthochlorobenzenesyndiazosulphonate* is anhydrous. It is deep red, and more soluble than the para-derivative, being also the most stable of these salts; the *anti*-compound forms yellow needles.

The degree of purity of a preparation of potassium benzenesyndiazosulphonate is indicated by titration with iodine solution, this process yielding good results when performed rapidly; the halogenised *syn*-salts, although more stable, are less soluble in water, and the results are not therefore so satisfactory, in consequence of polymerisation taking place.

The author points out the analogy existing between the potassium salt of mercury sulphonic acid, $Hg(SO_3K)_2$, and the stereoisomeric diazo-salts. Cryoscopic determinations indicate that both the latter are resolved on solution into the ions $PhN{:}N\cdot SO_3$ and K; they are, therefore, structurally identical, because a salt having the form of a true sulphite would dissociate into the ions $PhN{:}N$, SO_3, and K. Moreover, under this condition, the solutions would be colourless, which is not the case with the salts in question.

On these additional grounds, the author adheres to the conclusion that the isomerism exhibited by the two potassium benzenediazosulphonates is geometrical in character. M. O. F.

Parachlorometasulphobenzoic acid and its Derivatives. By H. M. Ullmann (*Amer. Chem. J.*, 1894, **16**, 530—543).—This acid is best prepared by distilling sulphuric anhydride from fuming sulphuric acid directly into a receiver containing the dried powdered parachlorobenzoic acid; the mixture is heated occasionally for some hours, the excess of sulphuric anhydride is distilled off, and the product converted into the barium salt. On adding an equivalent quantity of sulphuric acid to this, the free acid, $SO_3H\cdot C_6H_3Cl\cdot COOH + 3H_2O$, is obtained; it crystallises from water in long needles, and forms a dimorphous barium salt, both varieties of which contain $3H_2O$. On heating the acid with phosphorous pentachloride and ammonia successively, a product was obtained which proved not to be parachlorobenzoic sulphinide (compare Roode, Abstr., 1891, 1226), but a diamide. The sulphonic and carboxyl groups must therefore be in the meta-position, the acid having the constitution [COOH : SO_3H : Cl = 1 : 3 : 4]. The normal sodium salt, on treatment with two equivalents of phosphorous pentachloride, gives rise to the *dichloride*, $SO_2Cl\cdot C_6H_3Cl\cdot COCl$, which crystallises from light petroleum in flakes, and from ether in needles, and melts at 42—43°, and a *monochloride*, $SO_3H\cdot C_6H_3Cl\cdot COCl$, which is insoluble in cold, light petroleum, crys-

tallises from ether in needles, and melts at 163—167°. The *disulphonamide*, $SO_2NH_2 \cdot C_6H_3Cl \cdot CONH_2$, corresponding with the dichloride, crystallises from hot water in needles, and melts at 233°; the *dianilide* melts at 219—220°. G. T. M.

Ilicene. By A. Scheegans and E. Bronnert (*Arch. Pharm.*, 1884, **232**, 532—539).—*Ilicene*, $C_{35}H_{60}$, is a hydrocarbon obtained from the bark, wood and leaves of the common holly (*Ilex aquifolium*, Linn.); it crystallises from alcohol in silky bunches of thin, colourless needles, and melts at 182—183°; when distilled, even under diminished pressure, it decomposes. It is freely soluble in the usual organic solvents, but less soluble in cold glacial acetic acid and light petroleum, and insoluble in water. The molecular weight was determined by cryoscopic observations on the benzene solution. It appears to contain a methylene group, as the substance condenses with acid anhydrides to form acidyl derivatives. These crystallise in colourless needles or plates: *diacetylilicene* melts at 219·5°; *dipropionylilicene* at 209°; *dibenzoylilicene* at 188°. With hydrogen chloride and concentrated sulphuric acid, ilicene yields only resinous products, and it does not appear to form a picric acid derivative. On bromination, it yields a crystalline derivative of lower melting point; and on oxidation a mixture of acid and neutral substances.

Ilicene is undoubtedly identical with a substance isolated by Personne from bird-lime made from the inner bark of the holly, but which he erroneously described as an alcohol, ilicic alcohol, $C_{25}H_{44}O$ (Abstr., 1884, 1365). Jn. W.

Action of Acid Chlorides on Sodium Paranitrophenylnitrosamine. By O. Kühling (*Ber.*, 1895, **28**, 41—43).—Paranitrodiphenyl (m. p. 113—114°) is formed when an acid chloride acts on sodium paranitrophenylnitrosamine suspended in dry benzene. Employing toluene in place of benzene, 4 : 4′-*methylnitrodiphenyl* is obtained; this crystallises in yellowish-white prisms, and melts at 103—104°. M. O. F.

Constitution of Fluoresceïn. By C. Graebe (*Ber.*, 1895, **28**, 28—31).—Resorcinolphthaleïn is formed on heating fluoresceïn with fused caustic potash, and the diethylic ether, which melts at 175—176°, is obtained from phthalic anhydride and resorcinol diethylic ether; it is clearly, therefore, a derivative of orthobenzoylbenzoic acid, and from the fact that no anthraquinone-derivative is obtained on treating resorcinolphthaleïn or its ethers with dehydrating agents, it seems probable that the carbonyl group is situated between two hydroxyl groups.

On these grounds, the author represents the constitution of fluoresceïn by the formula, $CO<\underset{-O-}{C_6H_4}>{}^{1}C<\overset{2}{C_6H_3(OH)}\underset{2}{C_6H_3(OH)}>{}^{6}O$, pointing out, in support of this view, that the phthalins obtained from fluoresceïn and fluoresceïn chloride do not yield anthracene derivatives under the influence of concentrated sulphuric acid. The author attributes the

colour of fluoresceïn to its relationship with fluoran, which, although colourless, might be expected to yield coloured hydroxy-derivatives.

M. O. F.

Constitution of Fluoresceïn. By R. Nietzki and P. Schröter (*Ber.*, 1895, **28**, 44—56).—When the alkaline solution of fluorescin ethylic ether (Herzig, Abstr., 1892, 1319) is oxidised with potassium ferricyanide and acidified with glacial acetic acid, the *ethylic salt* of fluoresceïn, $C_{22}H_{16}O_5$, is obtained as a yellowish-brown precipitate. It separates from dilute alcohol or from glacial acetic acid in large crystals with a green lustre, and melts at 247°; the solution in caustic alkalis or alkali carbonates yields fluoresceïn when boiled. Bromine converts it into erythrin.

On heating the ethylic salt of fluoresceïn in alcoholic solution with sodium ethoxide (1 mol.) and excess of ethylic bromide, for some hours at 100°, the *ethylic ether*, $C_{24}H_{20}O_5$, is obtained; it crystallises from alcohol in dark yellow needles, which become orange-red when dried at 120—130°, and melt at 159°. Bromo-derivatives are obtained with difficulty; they are yellow dyes. This ether is identical with Baeyer's monethylic ether (*Annalen*, 1876, **183**, 1), which becomes colourless when recrystallised several times.

Fluoresceïn ethylic ether, $C_{22}H_{16}O_5$, obtained from the foregoing compound by the action of alcoholic potash, crystallises from dilute alcohol in yellow, rhombic plates which melt at 251°. Its solution in alkalis exhibits a green fluorescence which is less intense than that of fluoresceïn. The *bromo*-derivative is almost colourless, resembling Baeyer's eosin ethylic ether in this respect. The *acetyl* derivative melts at 222°.

The action of ethylic bromide on potassium fluoresceïn gives rise to the three ethers already described together with a colourless diethylic ether, which crystallises in long needles and melts at 183°. It is identical with Baeyer's diethylic ether (*loc. cit.*), and with the isofluoresceïn diethylic ether of O. Fischer and E. Hepp (this vol., i, 55). On reduction, it yields fluorescin diethylic ether which melts at 187°.

Fluorescin triethylic ether, $C_{26}H_{26}O_5$, is obtained by heating Herzig's diethylic ether (*loc. cit.*) with sodium ethoxide and ethylic bromide for some hours at 100°. It crystallises in colourless needles which melt at 110°, and when it is boiled with alcoholic potash the diethylic ether is regenerated.

The theoretical bearing of these results is then considered.

M. O. F.

Phthaleïns of Orthosulphoparatoluic acid. By J. A. Lyman (*Amer. Chem. J.*, 1894, **16**, 513—528).—*Phenylparamethylsulphophthaleïn*, $\begin{matrix} C_6H_3Me \\ | \\ SO_2—O \end{matrix}\!\!>\!C(C_6H_4\cdot OH)_2$, is obtained on gradually heating a mixture of carefully dehydrated orthosulphoparatoluic acid (1 mol.) and crystallised phenol (2 mols.) to 170°. It is a dark red, amorphous powder, slightly soluble in alcohol, ether, and chloroform, and in warm glacial acetic acid. It dissolves in solutions of alkali carbonates and hydroxides forming a red liquid. With bromine, it

appears to form a tribromo-derivative, $C_{20}H_{13}Br_3O_5S$, and it yields no pure product with phosphorus pentachloride.

When catechol, quinol, and pyrogallol are separately heated with orthosulphoparatoluic acid, phthaleïns appear to be formed, but none was isolated in a pure state. Resorcinol and orthosulphoparatoluic acid appear to yield hexaresorcinolparamethylsulphophthaleïn and octoresorcinolparamethylsulphophthaleïn, but these are not well-characterised substances. G. T. M.

Orcinolsulphophthaleïns. By J. E. Gilpin (*Amer. Chem. J.*, 1894, **16**, 528—530; compare preceding abstract).—Diörcinolsulphophthaleïn is obtained on heating together orcinol (2 mols.) and orthosulphobenzoic acid (1 mol.) at 180°. It is a dark red powder giving a red and green fluorescence in alkaline solution. It is insoluble in water, but dissolves sparingly in alcohol and ether. Attempts to prepare a tetraorcinolsulphophthaleïn by increasing the proportion of orcinol were without success. G. T. M.

Derivatives of Auramine. By J. Finckh and M. Schwimmer (*J. pr. Chem.*, 1894, [2], **50**, 401—445).—*Paramidophenylauramine*, $NH_2{\cdot}C_6H_4{\cdot}N{:}C(C_6H_4{\cdot}NMe_2)_2$, obtained by heating the auramine base with paraphenylenediamine, forms small, golden yellow, lustrous scales, melting at 221—222°. It is moderately soluble in hot alcohol, and is readily decomposed when hydrochloric acid is added to this solution, paraphenylenediamine and tetramethyldiamidobenzophenone being formed. The *hydrochloride* could not be obtained in the crystalline form, but only as an amorphous mass which melts at 224°. The *platinochloride* is a dark brown, granular powder, whilst the *picrate* melts at 185—186° (corr.). The *diacetyl* derivative, obtained by the action of acetic anhydride on the base, is a fine, ochre-yellow powder which melts at 194—195°. When it is heated with carbon bisulphide at 130°, tetramethyldiamidothiobenzophenone is produced along with *diacetamidophenylthiocarbimide*, $NAc_2{\cdot}C_6H_4{\cdot}NCS$, which crystallises in reddish, odourless scales melting at 195°. This substance readily combines with aniline to form *diacetylamidophenylthiocarbamide*, $NAc_2{\cdot}C_6H_4{\cdot}NCS{\cdot}NHPh$, a compound which crystallises in silver-white, lustrous plates and melts at 220—221°. *Triacetylparamidophenylauramine* is formed in small quantity along with the diacetyl compound. It crystallises in microscopic, greyish-yellow plates which melt at 257—258°. Boiling alcohol converts it into the diacetyl compound, whilst carbon bisulphide produces the diacetamidophenylthiocarbimide already described. *Monobenzoylparamidophenylauramine* forms orange-red prisms, and melts at 117°. The *dibenzoyl* derivative crystallises in hair-like needles, and melts at 180—181°.

The benzoyl derivatives are accompanied by a small amount of a sparingly soluble substance melting at 326—327°, which has the composition $C_{16}H_8NO$, and is decomposed by hydrochloric acid at 150° with formation of tetramethyldiamidobenzophenone and benzoic acid. It was found impossible to prepare the corresponding thiocarbimides from the benzoyl derivatives. *Paramidophenylauramine-*

phenylthiocarbimide, $C_{30}H_{31}N_5S$, obtained by the direct union of its constituents, forms slender, yellow needles melting at 124—127°.

Paraphenylenediauramine, $C_6H_4[N{:}C(C_6H_4{\cdot}NMe_2)_2]_2$, is obtained by heating paraphenylenediamine with 2 molecular proportions of auramine. It separates from xylene as a brownish-yellow, crystalline powder, melts at 311—312°, and decomposes at a higher temperature. Hydrochloric acid decomposes it in a similar manner to the monauramines, and carbon bisulphide reacts with it to produce tetramethyldiamidothiobenzophenone and paraphenylenethiocarbimide.

Orthamidophenylauramine, prepared by the use of orthophenylenediamine, forms orange-yellow crystals and melts at 199—200°. The *picrate*, $C_{23}H_{26}N_4,C_6H_3N_3O_7$, melts at 220—221°. *Benzoylorthamidophenylauramine* crystallises in slender, sulphur-yellow needles melting at 236—237°. The base is a primary amido-compound, and not a diimide, since it only reacts with 1 mol. of phenylthiocarbimide, forming *orthamidophenylauraminephenylthiocarbimide*, which is a yellow, crystalline powder melting at 166—167°.

Orthophenylenediauramine may be obtained by the action of orthamidophenylauramine on auramine, but is best prepared in a similar manner to the para-compound. It crystallises from xylene in slender, golden-yellow needles melting at 305°.

Benzoylauramine, $NBz{:}C(C_6H_4{\cdot}NMe_2)_2$, is readily formed, and crystallises in long, yellow needles which melt at 179° (corr.), and are not decomposed by continued boiling with water. Acetic acid produces a bluish-violet coloration, whilst sulphuric acid, added to an alcoholic solution, gives a blue coloration. The benzoyl derivative seems not to react with carbon bisulphide.

Auramine, as well as the substituted auramines, forms additive compounds with the thiocarbimides.

Auraminephenylthiocarbimide, $C_{24}H_{26}N_4S$, crystallises from xylene in microscopic, yellow needles, and melts at 194—195°. Its molecular weight in naphthalene solution is only one-half of that corresponding with the formula given. Dilute acids decompose it, with formation of tetramethyldiamidobenzophenone and phenylthiocarbamide. The thiocarbimide compound undergoes a somewhat complicated reaction when heated with carbon bisulphide at 150°, the products being auramine thiocyanate, tetramethyldiamidothiobenzophenone, phenylthiocarbimide, and thiocarbanilide.

Auraminemethylthiocarbimide, $C_{19}H_{24}N_4S$, forms odourless, yellow needles, and melts at 203—203·5°. *Auramine-ethylthiocarbimide* also forms yellow crystals melting at 179°. *Auramineallylthiocarbimide* crystallises in yellow prisms, and melts at 160—161°. Carbon bisulphide reacts with it in the same way as with the corresponding phenyl derivative. A. H.

Pine Tar. By A. Renard (*Compt. rend.*, 1894, **119**, 652—654).—In addition to the terebenthene previously described (Abstr., 1894, i, 612), pine tar contains a new hydrocarbon, $C_{14}H_{22}$, which boils at 250—280°. After purification by distillation over sodium, it boils at 254—257°; sp. gr. at 0° = 0·9419; refractive index, 1·507. It is a colourless, optically inactive liquid, which rapidly becomes brown

when exposed to air, but is not altered by hydrochloric acid. Bromine attacks it with great violence, forming a colourless, tetrabromo-derivative, $C_{14}H_{18}Br_4$, which crystallises from chloroform, but in presence of carbon bisulphide, an unstable dibromide, $C_{14}H_{22}Br_2$, is obtained. When the hydrocarbon is passed through a tube heated to dull redness, a small quantity of heptinine is formed. When treated with fuming nitric acid in presence of acetic acid, it yields a nitro-derivative, $C_{14}H_{21}NO_2$.

When the hydrocarbon is mixed with twice its volume of ordinary sulphuric acid, there is development of heat, and it is partly converted into a sulphonic derivative, and partly into viscous polymerides, which, when distilled in steam, yield a hydrocarbon boiling at 250—260°, and if the latter is treated with fuming sulphuric acid until no more of it dissolves, a hydrocarbon, $C_{14}H_{26}$, boiling at 250—253°, is obtained; this is not affected by fuming sulphuric acid, fuming nitric acid, or bromine in the cold. The sulphonic acid is a gummy substance, soluble in water, alcohol, or ether, and precipitated from its aqueous solutions by sulphuric or hydrochloric acids or sodium chloride. Its ammonium salt is very soluble in water, and yields a fluorescent solution, from which it is precipitated as a gummy mass by sodium chloride. The barium salt, $Ba(C_{14}H_{21}SO_3)_2$, is insoluble in water.

If the hydrocarbon, $C_{14}H_{22}$, is gently heated with a mixture of sulphuric acid and alcohol, a distinct blue coloration appears, and this reaction, according to Maquenne, is characteristic of the hydrides of benzene and its homologues. The other properties of the hydrocarbon also indicate that it is related to these hydrides, and it may be regarded as diheptenyl $(C_7H_{11})_2$, or ditolyl octohydride, $C_7H_{11}\cdot C_7H_{11}$. C. H. B.

Reuniol. By A. Hesse (*J. pr. Chem.*, 1894, [2], **50**, 472—479).—Oil of geranium, from the island of Réunion, contains a terpene-alcohol which is different from geraniol. It may be obtained by heating the oil with alcoholic potash at 100°, to decompose the ethereal salts which it contains, and then etherifying the alcoholic constituents by heating with camphoric anhydride. The non-alcoholic substances present may then be removed by distillation with steam, and the alcoholic constituents thus left in a state of greater purity. Reuniol obtained in this way boils at 225·5—226°, has sp. gr. = 0·865 at 20°, and the rotatory power of 1° 45′ (100 mm. tube). Its formula is probably $C_{10}H_{18}O$, although the numbers obtained by analysis do not agree very sharply with this, probably owing to the presence of water, which is very difficult to remove. The *acetate* boils at 124—125° (17 mm.), and has sp. gr. = 0·899 at 20°. Reuniol does not appear to form a definite compound with calcium chloride, and can thus be separated from geraniol. It has been detected in geranium oil from many sources, the French, African, and Spanish oils all being found to contain it. A substance possessing very similar properties has been described by Barbier (this vol., i, 4), who, however, does not seem to have obtained it free from non-alcoholic impurities. A. H.

Hydroxymethylene Compounds from Ketones of the Terpene Series. By O. WALLACH (*Ber.*, 1895, **28**, 31—34; compare L. Claisen, this vol., i, 62).—The formation of hydroxymethylene compounds from carvone, thujone, and hydrocarvone, indicates the presence of the group $-COMe$ in these ketones; fenchone, on the other hand, does not yield a derivative.

Hydroxymethylenecarvone, $C_8H_{12}<\begin{matrix}C{:}CH{\cdot}OH\\ |\\ CO\end{matrix}$, is prepared by the action of sodium and amylic formate on an ethereal solution of *d*-carvone. It boils at 132° under a pressure of 12 mm., and decomposes very readily on exposure to air; an intense violet-red coloration is developed by ferric chloride.

Hydroxymethylenethujone, $C_{11}H_{16}O_2$, is obtained from thujone in a similar manner; it melts at 40°, and boils at 115—118° (16 mm.).

The isomeride of camphor, obtained by heating the product of the oxidation of terpineol, $C_{10}H_{20}O_3$, with dilute sulphuric acid (Abstr., 1894, i, 44), also gives rise to a hydroxymethylene compound.

M. O. F.

Camphoric Acid. By W. A. NOYES (*Amer. Chem. J.*, 1894, **16**, 500—511; compare Abstr., 1894, i, 339).—The dihydroamidocampholytic acid, previously obtained (*loc. cit.*), forms the following derivatives. A *hydrochloride*, which crystallises from hot, concentrated solutions in long, stout needles, and melts and decomposes at 261—262°; the crystals show no tendency to a concentric grouping, and in this respect differ very markedly from those of the hydrochloride of the isomeric amidolauronic acid (m. p. 303—305°). The *nitrate* crystallises in long needles, and melts with decomposition at 212—213°; the *platinochloride*, in dark, orange-red plates.

Attempts to obtain an amine by distilling dihydroamidocampholytic acid with quicklime, resulted in the formation of an inner *anhydride* of the acid, having the formula, $C_8H_{14}<\begin{matrix}CO\\ |\\ NH\end{matrix}$. It is a wax-like substance, melts at 188—189°, boils without decomposition at 285—287°, and dissolves readily in ordinary solvents.

Campholytic acid forms a dibromide, which melts at 113—114° (compare Walker, Trans., 1893, 499), and is decomposed by ammonia and sodium carbonate, giving an oil which is insoluble in acids and alkalis. It forms insoluble zinc and silver salts (compare Walker, *loc. cit.*). The former is obtained in a semi-crystalline form when a solution of zinc chloride is added to a solution of the sodium salt.

Amidolauronic acid is obtained on heating α-camphoramic acid with sodium hypobromite in the same way as dihydroamidocampholytic acid is obtained from β-camphoramic acid, and is best isolated by conversion into the *hydrochloride*. The latter crystallises from water in well-defined needles, which have a strong tendency to form concentric groups; it melts at 303—305°, and is more sparingly soluble than the isomeric hydrochloride of dihydroamidocampholytic acid. The *platinochloride*, $(C_9H_{17}NO_2)_2,H_2PtCl_6$, crystallises in orange-red, microscopic, six-sided plates, and is more sparingly soluble than its

isomeride. The *anhydride* in most respects resembles its isomeride, but melts at 203°.

The study of the products of decomposition of the hydrochloride of amidolauronic acid by sodium nitrite is not yet complete, but the author regards his work as being in accordance with the supposition made by Walker, that camphoric acid contains the group COOH·ĊH·ĊR·COOH, and with the relative position ascribed to the carbonyl and methylene groups in the formula for camphor proposed by Armstrong. G. T. M.

Camphoronic acid and its Optical Isomerides. By O. Aschan (*Ber.*, 1895, **28**, 16—21).—Ordinary camphoronic acid, $C_9H_{14}O_6$, is lævorotatory, having $[\alpha]_j = -26{\cdot}9$; it melts and evolves gas at 158°, and 16·9 parts of it dissolve at 20° in 100 parts of water. Dextrorotatory camphoronic acid was prepared from the residues in the preparation of *l*-camphoric acid from *l*-borneol, from 90 grams of which, after a tedious process of purification, 6 grams of the acid were obtained. It has $[\alpha]_j = +27{\cdot}05$; it melts at 158—159°, gas being evolved; 16·74 parts dissolve in 100 parts of water at 20°; in appearance it resembles the *l*-isomeride, and a like resemblance is exhibited by the isomeric calcium salts, which both contain $8H_2O$ when dried in a vacuum, $12H_2O$ when dried in the air. When the two isomeric acids are mixed in aqueous solution, the inactive racemic acid is formed; this has quite different properties. It crystallises in large, square plates, instead of in needles; melts at 172°; and dissolves only to the extent of 3·72 parts in 100 of water at 20°; the barium salt is very soluble in water, whereas the barium salts of the two active acids are almost insoluble.

By the action of bromine on camphoronic chloride, a compound is obtained which is probably $COOH{\cdot}C_9H_{10}Br{\cdot}(CO)_2{\cdot}O$, being both an acid and an acid anhydride; it melts at 158°. Boiling water removes hydrogen bromide from it, yielding a (? lactonic) acid, melting at 208—209°; another acid melting at 240° is formed in addition. It also yields an anil melting at 171—172°. These compounds are undergoing further investigation. C. F. B.

Balsam of Tolu. By P. Oberlaender (*Arch. Pharm.*, 1894, **232**, 559—600).—Balsam of Tolu consists almost entirely of a mixture of ethereal salts of benzoic and cinnamic acids; partly (7·5 per cent.) the benzylic salts, with which a little vanillin is associated, the rest those of a resin alcohol; this alcohol is prepared from the ethereal solution of the balsam by first extracting the resinous salts with cold alkali and precipitating them with carbonic anhydride, and then repeatedly hydrolysing them with alkali, the alcohol being precipitated after each dissolution with hot hydrochloric acid. The final purification is effected by repeated precipitation with acid from ammoniacal solution.

Toluresinotannol, $C_{17}H_{18}O_5$, a lower homologue of peruresinotannol, is a dark brown, neutral powder, having no taste or odour; it does not soften when heated, but decomposes at 100° without melting (the balsam melts at 65°). It is closely related to the tannins, as it gives

colour reactions with ferric chloride and potassium dichromate, and precipitates with lead acetate and gelatin; a characteristic black coloration is obtained with hydrochloric acid. The molecule contains a hydroxyl group, as the tannol forms alkali and acidyl derivatives; it also contains a methoxy-group, removable by hydriodic acid; the constitutional formula is therefore $OH{\cdot}C_{16}H_{14}O_3{\cdot}OMe$. As the acidyl derivatives do not show the above phenolic reactions, and the tannin does not interact with phenylhydrazine or hydroxylamine, the remaining oxygen is neither in the ketonic nor the aldehydic nor the hydroxylic form. On oxidation, reduction, and bromination, the tannin yields indefinite products; with nitric acid, however, picric and oxalic acids are obtained. When fused with caustic potash, it yields acetic and protocatechuic acids and a trace of valeric acid; when distilled with zinc dust, low phenols and naphthalene. The *potassium* derivative, $C_{17}H_{17}KO_5$, forms white, amorphous flocks. The *acetyl* derivative, $C_{17}H_{17}AcO_5$, is an ochre-yellow, crystalline powder; like the other acidyl derivatives, it is hydrolysed into its proximate constituents by alkalis. The *benzoyl* derivative is a yellowish-brown, amorphous powder; the *cinnamoyl* derivative, a greyish-brown powder, which does not resemble the original resin. JN. W.

The Sugar of Indican. By C. J. VAN LOOKEREN (*Landw. Versuchs-Stat.*, 1894, **45**, 195—200).—The author previously expressed the opinion (this vol., i, 96) that the sugar obtained from indican, which Schunck calls indiglucin, is dextrose; this is now shown to be the case. Owing to the great ease with which indican decomposes, it was found best to treat the fresh sap of indigofera leaves with sulphuric acid. The resulting sugar was identified as dextrose by means of the osazone, its rotatory power, and its reaction with nitric acid. A small quantity of levulose was also found, but this was present in the fresh sap. N. H. J. M.

Randia Dumetorum. By M. VOGTHERR (*Arch. Pharm.*, 1894, **232**, 489—532).—The fruit of the bushy gardenia (*Randia dumetorum*, Lamarck) is in popular use in India, where the plant is known as *Gelaphal*, as an emetic and remedy for dysentery. In addition to the substances described later, a minute quantity of an alkaloïd was isolated, but not characterised or identified, and a small amount of lead (0·02 per cent.) was invariably present.

Randiasaponin, a glucoside, forms yellowish plates, or a white, amorphous powder, and melts and decomposes at about 250°. It loses 11·4 per cent. of water at 100°; the percentage composition of the dry substance is C, 55·52; H, 8·72; O, 35·76. It is not hygroscopic, but dissolves in water to a neutral solution, which froths readily. It is reprecipitated from this solution by moderately strong hydrochloric or sulphuric acid, and is also thrown down by lead acetate and basic acetate as a gelatinous compound, which serves for its purification. It does not reduce alkaline copper solution, except after prolonged hydrolysis with dilute hydrochloric acid, when it is converted into randiasapogenin and two *sugars*. The *osazone* of one of these is insoluble in ether, crystallises in yellow crusts, and melts

at 166—167°, whilst that of the other is soluble in ether and amorphous, and melts at 176—177°. Randiasaponin, like quillayasapotoxin, has the property of dissolving red blood corpuscles to a clear solution.

Randiasapogenin, $C_{26}H_{50}O_9$(?), the product of the hydrolysis of randiasaponin, forms a friable mass, little soluble in water. It decomposes without melting, the chief product being a substance crystallising in colourless needles. Moist randiasapogenin dissolves in strong sulphuric acid to a yellow solution, which shows a characteristic green fluorescence.

Randic acid, $C_{30}H_{52}O_{10}$, appears to be a monobasic acid of the series $C_nH_{2n-8}O_{10}$, characterised by Kobert as the saponin series, and exists, apparently, in loose combination with randiasaponin. It crystallises from alcohol in white, nodular masses, and melts at 208—210°. It is sparingly soluble in water and ether, freely in alcohol, acetic acid, and concentrated sulphuric acid; solutions of the alkali salts froth very readily. The *potassium* salt is insoluble in alcohol. The *calcium*, *barium*, *ferrous*, *ferric*, *copper*, *lead*, *mercurous*, and *mercuric* salts are mentioned. Randic acid resembles quillayic acid in dissolving red blood corpuscles without destroying the colouring matter, and in precipitating albumins and peptones. To these properties, and the similar property of randiasaponin, the poisonous character of the fruit is probably due.

Randiatannic acid exists in small quantity in the pericarp, and is a brown, very hygroscopic mass, which is freely soluble in ether, as well as in water and alcohol. It gives a green coloration with ferric chloride, and a yellow precipitate with basic lead acetate, and reduces alkaline copper solution.

One of the products of the decomposition of randiatannic acid appears to be *randia-red*, $C_{33}H_{34}O_{26}$, a substance to which the brown colour of the pericarp of the fruit is due; this is precipitated by acids from the alkaline extract as a brown powder, which is insoluble in water, alcohol, and ether, but easily soluble in alkalis. The solutions give reddish precipitates with lead acetate and alum. A brownish-red colouring matter, probably the *ammonium*-derivative, is precipitated by ammonia from the acid mother liquor; it forms a harsh mass resembling asphalt, and is soluble in hot water; it is decomposed by caustic soda with evolution of ammonia.

Randia fat is a yellowish-green substance of the consistence of butter; it melts at 28—29°, and its sp. gr. is 0·9175 at 20°. The acid number is 13·8; the ester number, 146·4; the saponification number, 160·2; and the iodine number, after two hours, 43·24.

JN. W.

Halogenised Amines. By S. GABRIEL and T. POSNER (*Ber.*, 1894, **27**, 3509—3525).—When orthamidobenzylic alcohol (15 grams) is heated with fuming hydrobromic acid (40 c.c.) for an hour at 100°, the *hydrobromide* of orthamidobenzylic bromide,

$$CH_2Br{\cdot}C_6H_4{\cdot}NH_2,HBr,$$

is formed. The *hydrochloride* of orthamidobenzylic chloride is prepared in a similar manner, but neither salt yields the free base on

treatment with alkali, a colourless precipitate of orthobenzyleneimide, $(C_7H_7N)_x$ being thrown down.

μ-Methylphenopentoxazole, $C_6H_4<\begin{matrix}CH_2\cdot O\\ |\\ N=CMe\end{matrix}$, is obtained in the form of the *hydrobromide* when the hydrobromide of orthamidobenzylic bromide is heated for a few minutes with acetic anhydride; the salt melts at 170—172°, and has an acrid taste. The free base is a yellow oil, which rapidly decomposes when distilled alone or in a current of steam, but a portion remains unchanged and boils at 230°; the *picrate* melts at 146—149°. Methylphenopentoxazole hydrobromide in aqueous solution undergoes spontaneous conversion into the hydrobromide of orthamidobenzylic acetate (Söderbaum and Widman, Abstr., 1889, 972), of which the *picrate* crystallises in short prisms and melts at 99°.

μ-Methylphenopenthiazole, $C_6H_4<\begin{matrix}CH_2\cdot S\\ |\\ N=CMe\end{matrix}$, is obtained by the action of phosphorus pentasulphide on the hydrobromide of methylphenopentoxazole; it melts at 45—46°, and boils at 265—267° under a pressure of 771 mm. It is also obtained by heating orthamidobenzylic chloride hydrochloride or orthamidobenzylic alcohol with acetic anhydride, and subsequent treatment with phosphorus pentasulphide; the same base is produced on heating a mixture of the hydrochloride of orthamidobenzylic chloride and thioacetamide for a quarter of an hour at 100°. The *platinochloride* forms orange-yellow needles, and the *dichromate* crystallises in lustrous, reddish-yellow needles; the *picrate* blackens at 170° and melts at 178°. Orthamidobenzylic sulphide is formed when methylphenopenthiazole is heated with fuming hydrochloric acid for two hours at 180°; it melts at 81—82°. The *formyl* derivative crystallises in snow-white needles which melt at 163°, and the *acetyl* derivative forms silky needles which melt at 209°; when this substance is heated on the water bath with phosphorus pentachloride, methylphenopenthiazole is formed.

μ-Ethylphenopentoxazole, $C_6H_4<\begin{matrix}CH_2\cdot O\\ |\\ N=CEt\end{matrix}$, is obtained similarly to the methyl derivative from orthamidobenzylic bromide and propionic anhydride. The *picrate* melts at 138—139°.

Orthobenzamidobenzylic chloride is formed when the hydrochloride of orthamidobenzylic chloride is added to benzoic chloride which is nearly boiling; it separates from alcohol in silky needles which melt at 124—125°. When this substance is heated with phosphorus pentasulphide, *μ-phenylphenopenthiazole*, $C_6H_4<\begin{matrix}CH_2\cdot S\\ |\\ N=CPh\end{matrix}$, is formed; it crystallises from methylic alcohol in yellowish needles which melt at 55—58°, and the *picrate* melts at 176—177°. The base is also obtained by heating a mixture of the hydrobromide of orthamidobenzylic bromide and thiobenzamide at 100°.

Orthobenzamidobenzylaniline, $NHPh\cdot CH_2\cdot C_6H_4\cdot NHBz$, is formed on heating orthamidobenzylic chloride with aniline; it crystallises in colourless needles which melt at 113—114°. This substance is isomeric with orthamidobenzylbenzanilide, which melts at 119°.

The following halogenised amines will form the subject of a later communication—*β-chloro-*, *β-bromo-*, and *γ-chloro-butylamine*, *γ-chloro-*, and *γ-bromo-hexylamine*. M. O. F.

Derivatives of Furazan. By L. Wolff (*Ber.*, 1895, **28**, 69—74).—The author has succeeded in preparing the anhydrides of dimethylglyoxime and methylglyoximecarboxylic acid, although Hantzsch (Abstr., 1892, 693) and Nussberger (Abstr., 1892, 1175) were unable to obtain these compounds. *Dimethylfurazan*, $O<\begin{matrix}N{:}CMe\\ |\\ N{:}CMe\end{matrix}$, is formed when dimethylglyoxime is boiled with aqueous soda, but is best prepared by heating it with water at 160°. It is a colourless liquid of sp. gr. 1·054 at 15°, boils without decomposition at 156°, and when cooled solidifies to a crystalline mass, melting at −7°. It is volatile with steam, and is exceptionally stable towards acids and alkalis. When treated with potassium permanganate in presence of sulphuric acid, it is converted into *methylfurazancarboxylic acid*, $O<\begin{matrix}N{:}C\cdot COOH\\ |\\ N{:}CMe\end{matrix}$, which crystallises with $1H_2O$ in large, lustrous plates, melting at 39°. The anhydrous acid melts at 74°, and absorbs water from the air. The *calcium* salt crystallises in plates, the *silver* salt in needles. Methylfurazancarboxylic acid is converted, by oxidation with potassium permanganate, into *furazandicarboxylic acid*, $O<\begin{matrix}N{:}C\cdot COOH\\ |\\ N{:}C\cdot COOH\end{matrix}$, which crystallises in large, vitreous prisms, melting and evolving gas, at 178°. The *calcium* salt crystallises in white, lustrous needles, whilst the *silver* salt is a crystalline powder. Both the acid and its salts very readily decompose when they are boiled with water, carbonic anhydride being evolved, and cyanoximidoacetic acid formed. The following reactions are due to this change. The colourless solutions of the calcium and alkali salts become yellow when boiled, and then give a yellow precipitate with silver nitrate solution. Copper acetate produces no precipitate, but, when the blue solution is boiled, it becomes green, and deposits crystals of copper cyanoximidoacetate.

Methylethylfurazan is a mobile, neutral liquid, boiling at 170·5°.

The author has made a number of unsuccessful attempts to convert dimethylglyoxime into an isomeric compound by the action of hydrogen chloride in various solvents, of caustic soda, and of sulphuric acid. A. H.

Phenyl-Derivatives of Pyrazole. By E. Buchner (*Ber.*, 1894, **27**, 3247—3250).—In conjunction with Dessauer and Fritsch (Abstr., 1893, i, 281, 282), the author has shown that two phenylpyrazoles, melting at 228° and 78° respectively, are obtained from ethylic diazoacetate and ethylic cinnamate, in both of which the phenyl group is combined with a carbon atom. These were regarded as 5- and 4-pyrazoles, but recent syntheses of the latter by Knorr and Sjollema (Abstr., 1894, i, 546) have shown that it must be either 3- or 5-pyrazole. Knorr and Sjollema regard the compound melting at 228° as the 4-derivative, its synthesis by Rothenburg from hydrazine hydrate

and benzoylacetaldehyde, however, is not in agreement with this supposition, but shows that this also must be a 3- or 5-derivative; this is also borne out by the fact that the corresponding dicarboxylic acid, when heated with resorcinol, gives a fluorescent solution on the addition of ammonia. A definite decision as to which is the 3-derivative and which the 5-derivative is not at present possible, but the author does not agree with Knorr's view (Abstr., 1894, i, 543), that the positions 3- and 5- in the pyrazole ring are identical. H. G. C.

Action of Phenylhydrazine on Ethylic Ethoxymethylenemalonate. By L. Claisen and E. Haase (*Ber.*, 1895, **28**, 35—41).—This condensation gives rise to the *phenylhydrazide*,

$$NHPh\cdot NH\cdot CH{:}C(COOEt)_2,$$

which melts at 112°. When this substance is heated in an oil bath at 170—175°, the ethylic salt of 1 : 5 : 4-phenylpyrazolonecarboxylic acid is formed (compare Ruhemann and Morrell, Trans., 1892, 793). On boiling this salt for some hours with aqueous caustic soda (3 mols.), 1 : 5-phenylpyrazolone is formed, which melts at 118—119°.

1 : 5-Phenylpyrazolone closely resembles Knorr's 1 : 3 : 5-phenylmethylpyrazolone in properties. The *hydrochloride* melts at 165°; the *benzylidene-* and *isonitroso*-derivatives melt at 170° and 160° respectively.

The constitution of 1 : 5-phenylpyrazolone has been the subject of recent discussion, and the author shows that it is best represented by the formula $\begin{matrix} NPh\cdot CO \\ | \\ N=CH \end{matrix}\!>\!CH_2$, already put forward by Stolz.

M. O. F.

Derivatives of Tetrazole. By M. Freund and H. Hempel (*Ber.*, 1895, **28**, 74—81).—4-Phenylthiosemicarbazide is a base, and forms a *hydrochloride*, which crystallises in compact needles, melting at 169°. When this is dissolved in dilute acid and treated with potassium nitrite solution, a compound, which is probably *4-phenyl-3-thiotetrazoline*, $N\!<\!\begin{matrix} N-NPh \\ | \\ NH\cdot CS \end{matrix}$, is precipitated. It crystallises from alcohol in compact needles, which decompose violently at 142—145°. It dissolves in aqueous alkalis when gently heated, and can be recovered by the addition of acid; if, however, the solution be more strongly heated, the isomeric phenyltetrazolethiole is formed. Ammoniacal silver oxide added to an alcoholic solution of the tetrazoline produces the silver salt of the isomeric tetrazole.

4-Phenyltetrazole-3-thiole, $N\!<\!\begin{matrix} N\cdot NPh \\ | \\ N{:}C\cdot SH \end{matrix}$, crystallises in slender, matted needles, which decompose at 147—150°. It dissolves without alteration in cold sulphuric acid or boiling hydrochloric acid. The *silver* salt, CN_4PhSAg, is an amorphous, white mass. When treated with methylic iodide, it is converted into *phenyltetrazolemethylthiole*, $CN_4Ph\cdot SMe$, which crystallises in cubes, melting at 84°. The same compound is obtained when the tetrazole is heated with sodium ethoxide and methylic iodide. When oxidised with potassium permanganate, the tetrazole is converted into *4-phenyltetrazole-3-sulphonic*

acid, of which the *potassium* salt, CN_4Ph,SO_3K, is soluble in alcohol and melts at 242°.

4-*Phenyl*-3-*hydroxytetrazole*, $CN_4Ph{\cdot}OH$, accompanies the sulphonic acid just described. It crystallises from alcohol in slender, matted needles, melting at 185—186°. Its *potassium* salt, $C_7H_5N_4OK$, is also soluble in alcohol. Oxidation, by means of nitric or nitrous acid, ferric chloride, or hydrogen peroxide, converts the tetrazole into the corresponding *bisulphide*, $S_2(CN_4Ph)_2$, which forms flat, rhombic crystals, and decomposes at 145—148°. It is insoluble in cold aqueous alkalis, but dissolves in them on warming, reduction to the tetrazole taking place. A similar reduction also occurs when it is treated with ammoniacal silver oxide.

The relations of the tetrazoline and tetrazole compounds are best expressed by the formulæ given above, the existence of the mercaptan group in the tetrazole being proved by its behaviour on oxidation. It will be noticed that the two formulæ represent what are usually recognised as tautomeric forms of the same substance. A. H.

Vellosine: an Alkaloïd from Pereiro Bark ("Geissospermum Vellosii"). By M. Freund and C. Fauvet (*Annalen*, 1894, **282**, 247—267).—A preliminary investigation of the so-called geissospermine, manufactured by Trommsdorff (Abstr., 1893, i, 446), showed that this compound was not identical with Hesse's geissospermine (Abstr., 1880, 675). Hesse (Abstr., 1894, i, 155) believes that Trommsdorff's base is identical with a third alkaloïd previously isolated by him (*loc cit.*) from pereiro bark. There are, however, on the market, two sorts of pereiro bark: a thin, bast-like variety and a thicker kind; it is from the latter that Trommsdorff prepares his alkaloïd. Hesse has not stated which of the two varieties he worked with. The authors now propose the name *vellosine* for Trommsdorff's base, and *apovellosine* for the amorphous base obtained from it (Abstr., 1893, i, 466).

Vellosine, $C_{23}H_{28}N_2O_4$ (m. p. 189°), has already been partially described (*loc. cit.*). The base is soluble in chloroform and hot benzene, but insoluble in water, and dissolves in concentrated nitric acid with decomposition and the production of a purple-red coloration; it forms rhombic, hemihedral crystals,

$$a : b : c = 0{\cdot}9703 : 1 : 0{\cdot}6140,$$

has a specific rotatory power in a chloroform solution of about 10 per cent. concentration of $[\alpha]_D = +22{\cdot}8$ at 23°. Its molecular weight, determined by the ebullioscopic method, is in agreement with the above formula, and Zeisel's method reveals the presence of two methoxyl groups. As vellosine is easily converted into apovellosine by dilute acids (see below), heating must be avoided in the preparation of its salts. The *hydrochloride*, $C_{23}H_{28}N_2O_4,HCl + H_2O$, commences to soften at 170°, and melts in its water of crystallisation at 180° with frothing; subsequently, however, it again solidifies, and then melts and decomposes at 240°. If the salt is previously dehydrated at 120°, it melts at 245—248°. The *platinochloride* is a crystalline powder of melting point 80°; when heated with water, it

decomposes with the production of a violet coloration. The *hydrobromide* crystallises in lustrous needles with $1H_2O$; it melts at 194—195°, which value is the same for the anhydrous salt. The *hydriodide* crystallises with $1H_2O$, commences to soften at 210°, and melts at 217—218°. *Vellosine hydrogen sulphate*,

$$C_{23}H_{28}N_2O_4,H_2SO_4 + H_2O,$$

melts at 210°, and the *nitrate* decomposes at 225°. The *methiodide*, $C_{23}H_{28}N_2O_4.MeI$, melts at 264°.

Apovellosine, $C_{46}H_{54}N_2O_7$, is prepared by boiling a solution of vellosine in excess of hydrochloric acid of 1·1 sp. gr. for five minutes, and precipitating with soda; the base is amorphous, hygroscopic, very soluble in most organic solvents, and melts, according to the way it is heated, between 60° and 70°. If a trace of the base is dissolved in a drop of concentrated sulphuric acid containing some nitric acid, a beautiful violet colour is developed as the solution absorbs water: a solution in hydrochloric acid gives a carmine-red coloration on the addition of ferric chloride, which changes to violet on adding soda, but is destroyed by an excess of the latter. The formula given above for the base is supported by the ebullioscopic method; Zeisel's method shows that apovellosine contains four methoxyl groups. The *hydriodide*, $C_{46}H_{54}N_4O_7,4HI + 4H_2O$ sinters at 160°, and melts with decomposition at 253—254°. The *hydrobromide* (anhydrous) melts and decomposes at 210°; the *methiodide*, $C_{46}H_{54}N_4O_7,2MeI$, melts at 265°. The *nitrate* and *platinochloride* are unstable, and were not isolated.

Apovellosol hydrobromide, $C_{42}H_{46}N_4O_7,4HBr + 5H_2O$, is produced, together with methylic bromide and water, when vellosine is boiled with concentrated hydrobromic acid; it separates from hot water in stout crystals, and melts at 245°. A solution acidified with hydrochloric acid gives a beautiful, carmine-red coloration with ferric chloride, which, on the addition of soda, changes to violet and then vanishes; if the precipitated ferric oxide is now dissolved in acetic acid, a colourless solution is formed, which again becomes carmine-red on adding hydrochloric acid. When concentrated potash is added to a solution of the hydrobromide, an oil separates which is probably a potassium derivative of apovellosol. The *hydriodide* crystallises with $5H_2O$; this hydrate melts at 235°; a specimen crystallised from aqueous alcohol melted at 265°.

Apovellosidine, $C_{42}H_{54}N_4O_6$, obtained by evaporating a solution of apovellosine with potassium hydroxide, crystallises from alcohol in colourless needles, and melts at 154°; the compound contains four methoxyl groups. The *hydrobromide*, $C_{42}H_{54}N_4O_6,3HBr + 6H_2O$, melts at 235°; the *platinochloride* melts at 203°, and the *methiodide*, $C_{42}H_{52}N_4O_5,2MeI$, melts at 262°. When vellosine is heated with alkali, a compound melting at 145° is obtained; it is not identical with apovellosidine.

Vellosine is toxic, the lethal dose being 0·15 gram in the case of rabbits; death occurs by the weakening of the respiratory centre. A short account of the further physiological action of the base is given in the paper. A. R. L.

Cadaverine and Choline from Putrid Horseflesh. By W. GULEWITSCH (*Zeit. physiol. Chem.*, 1894, **20**, 287—305).—These two substances were obtained from putrid horseflesh in quantity, and a number of their compounds were prepared, and analysed. Among these may be mentioned the compound of cadaverine and mercuric chloride, $C_5H_{12}N_2,2HCl,4HgCl_2$; at 135°, this loses 18·33 per cent. of mercuric chloride. The platinochloride, $C_5H_{14}N_2,H_2PtCl_6$, was prepared. The crystalline form of different ptomaïne derivatives appears to vary a good deal.

The name *ptomatine* is suggested as more grammatically correct than ptomaïne. W. D. H.

Ash-free Albumin. By K. BÜLOW (*Pflüger's Archiv*, 1894, **58**, 207—221).—Ash-free albumin was prepared by Harnack's method from various proteïd sources; and although the original proteïds differ in their properties, the ash-free product does not. It is insoluble in water, and like amido-acids, it forms, with acids and bases, salts soluble in water; it appears to form, with bases, two categories of compounds.

The acid solutions are very sensitive to neutral salts, a small addition producing precipitation; the alkaline solutions are indifferent to neutral salts. In this direction, the sulphates of the alkali metals act most strongly, then the nitrates, then the chlorides. The specific rotatory power of proteïds is markedly altered by small admixtures of other substances. W. D. H.

Ferratin: its Dietetical and Therapeutical Employment. By O. SCHMIEDEBERG (*Chem. Centr.*, 1894, i, 741).—The iron compounds of albumin, like other iron compounds, are at once blackened by ammonium sulphide in alkaline solution. If, however, alkaline solutions of such iron albuminates are kept some time, or are heated for a short time, they are not at once blackened by ammonium sulphide, although they are blackened by it after the lapse of some time. Iron compounds which are not at once blackened by ammonium sulphide are obtained from many organic compounds which contain hydroxyl, such as tartaric acid, citric acid, mannitol, and glycerol. *Ferratin*, a "ferrialbuminic acid" containing 6 per cent. of iron, is obtained by boiling pig's liver with water, and adding tartaric acid to the cold filtrate. The ferratin contained in the liver is the source of iron for the formation of blood, and its disappearance from the liver can be detected in cases of deficiency of iron and loss of blood. Iron salts are, as a rule, difficult to assimilate; ferratin, however, after repeated doses, is not injurious either to the intestines or kidneys; and much larger quantities of iron may be injected directly into the blood in the form of ferratin than in the form of iron salts. E. C. R.

Organic Chemistry.

Sodionitroethane. By Victor Meyer (*Ber.*, 1895, **28**, 202—204).—The author traverses Nef's statements (this vol., i, 3). When sodionitroethane is decomposed with ice-cold, dilute sulphuric acid, it is converted to the extent of over 60 per cent. into nitroethane, and only a small quantity of nitrous oxide is evolved; if acetic acid is used, no nitrous oxide is evolved. It must thus be a true derivative of nitroethane, and cannot have a quite dissimilar constitution. C. F. B.

Hydration of Acetylene: Formation of Paraldehyde. By Alexandre Desgrez (*Bull. Soc. Chim.*, 1894, [3], **11**, 362—366).—Purified wood charcoal, at a moderate temperature, absorbs acetylene, and the latter, on treatment with water at 325°, is converted into an aldehyde, since the product restores the colour to reduced rosaniline. A better yield is obtained by heating acetylenedicarboxylic acid with water at 320—330° for half an hour; on distilling the product at a low temperature, a considerable quantity of a liquid passes over, which restores the colour to reduced rosaniline, and can be converted into silver acetate; as the temperature was above 40°, it was probably paraldehyde. On passing the more volatile portions of the product into a solution of ammonia in ether, a small quantity of aldehyde-ammonia was formed. Jn. W.

Hydration of Allylene. By Alexandre Desgrez (*Bull. Soc. Chim.*, 1894, [3], **11**, 391—394).—When tetrolic acid, CMe:C·COOH (from β-chlorocrotonic acid), is heated with water at 325—330° for half an hour, the liberated allylene is converted into acetone, which may be isolated by means of the sodium hydrogen sulphite compound, and recognised in the usual manner. At a higher temperature, mesitylic oxide is probably formed, but not propaldehyde. Jn. W.

Action of Reducing Agents on Potassium Nickelocyanide. By Thomas Moore (*Chem. News*, 1895, **71**, 81—82).—See this vol., ii, 168.

Preparation of Potassium Ferricyanide. By M. S. Walker (*Amer. Chem. J.*, 1895, **17**, 68).—Twenty-six grams of potassium ferrocyanide are dissolved in 200 c.c. of cold water, 8 c.c. of strong hydrochloric acid added, and then a solution of 2 grams of potassium permanganate in 300 c.c. of water until oxidation is complete. On neutralisating with chalk or barium carbonate, and evaporating, crystals of the pure ferricyanide are obtained. L. T. T.

Oxidation of Alcohols by Fehling's Solution. Transformation of Propionic into Lactic acid. By Fernand Gaud (*Compt. rend.*, 1894, **119**, 862—863, and 905—906).—Alcohols have no action

on Fehling's solution under ordinary conditions, but when they are heated together in sealed tubes at temperatures above 100°, the alcohols are oxidised, with formation of the corresponding aldehyde and acid when the alcohol is in excess, and of the corresponding acid only when the Fehling's solution is in excess. Cuprous oxide is precipitated in violet-red octahedra or cubes. In some cases copper also separates in microscopic prisms, terminated by quadratic pyramids.

In the case of ethylic alcohol, if the heating at 240°, with excess of Fehling's solution, is prolonged, a small quantity of cupric acetate is formed, and afterwards splits up into cuprous oxide, carbonic anhydride, and acetic acid; with methylic alcohol, a small quantity of cupric formate is formed and decomposes in an analogous manner; with propylic alcohol, small quantities of lactic acid and ethylidenelactic acid are formed. The reaction $2[Cu(C_3H_5O_2)_2] + 2H_2O = Cu_2 + 2C_3H_6O_3 + 2C_3H_5{\cdot}COOH$ is endothermic, and if cupric propionate is heated with water in sealed tubes at 180—200° for 60 hours, small quantities of metallic copper, cuprous oxide, and propionic and lactic acids are formed. C. H. B.

Secondary Allylic Alcohols. By H. Fournier (*Bull. Soc. Chim.*, 1894, [3], **11**, 359—362).—Several homologues of ethylallylcarbinol have been prepared by the interaction of allylic bromide and zinc with fatty aldehydes (Abstr., 1894, i, 19, 394). They are all colourless liquids of more or less disagreeable odour; the acetates, on the other hand, with the exception of the highest, have agreeable odours. The yield of the alcohols was from 25 to 30 per cent. of the theoretical; that of the acetates about 45 per cent. It is noteworthy that the refractive indices both of the alcohols and of the acetates increase by 0·003 for each increment of CH_2, and that the refractive indices of the acetates are uniformly 0·012 less than those of the corresponding alcohols.

Isopropylallylcarbinol, from isobutaldehyde, boils at 139—141°; the sp. gr. at 15° is 0·846, the refractive index $[\alpha]_D = 1{\cdot}435$. The *acetate* boils at 160—162°; the sp. gr. at 15° = 0·891, the refractive index $[\alpha]_D = 1{\cdot}423$. *Isobutylallylcarbinol*, from isovaleraldehyde, boils at 162—164°; the sp. gr. at 15° is 0·845, the refractive index $[\alpha]_D = 1{\cdot}438$. The *acetate* boils at 179—181°; its sp. gr. at 15° = 0·887, its refractive index $[\alpha]_D = 1{\cdot}426$. *Hexylallylcarbinol*, from œnanthaldehyde, is slightly viscous, and boils at 210—212°; the sp. gr. at 15° is 0·848, the refractive index $[\alpha]_D = 1{\cdot}444$. The *acetate* boils at 222—224°; the sp. gr. at 15° = 0·879, the refractive index $[\alpha]_D = 1{\cdot}432$. Jn. W.

Formation of Mannitol in Wines. By H. and A. Malbot (*Bull. Soc. Chim.*, 1894, [3], **11**, 413—415).—A continuation of previous work (Abstr., 1894, i, 269 and 295). The reduction of glucose may, perhaps, be due to the butyric ferment, which is known to liberate hydrogen, or, possibly, to the propionic ferment.

The presence of an unfermentable, difficultly hydrolysable sugar has been observed in a wine from which all glucose had been removed by fermentation. This sugar was transformed, in the course of some

months, into mannitol, but, in the presence of sulphurous acid, into glucose. Jn. W.

Trehalose in Mushrooms. By Emile E. Bourquelot (*Bull. Soc. Chim.*, 1894, [3], **11**, 353—356).—A claim for priority. The author (Abstr., 1889, 740; 1891, 103) has already obtained the whole of Winterstein's recent results (Abstr., 1894, i, 161). The latter misquotes him in asserting that he stated there is no trehalose in dried mushrooms; his observation was that the trehalose often disappears during the desiccation. Jn. W.

Blue Iodide of Starch and the Molecular Structure of "Dissolved" Starch. By Fritz W. Küster (*Annalen*, 1894, **283**, 360—379; compare F. Mylius, Abstr., 1887, 568).—Although neither dry nor dissolved starch takes up free iodine in any considerable quantity, the amount of the halogen in blue iodide of starch obtained from either source by treatment with iodine dissolved in potassium iodide, depends closely on the concentration of the solution. The results of numerous experiments lead the author to the conclusion that, contrary to the views of previous investigators, blue iodide of starch is neither a compound nor a mixture, but must be regarded as a well-defined, solid solution of iodine in starch; this confirms the opinion expressed by A. Meyer in a recent monograph.

Regarding its properties from this point of view, "dissolved" starch more closely resembles an emulsion than a solution.

M. O. F.

The Products of Hydrolysis of Fungus-cellulose. By Ernst Winterstein (*Ber.*, 1895, **28**, 167—169).—Cellulose prepared from the *Agaracineæ* (*Boletus* and *Agaricus*) and from *Helvellaceæ* (*Morchella*) has already (this vol., i, 80) been shown to yield glucosamine when heated with hydrochloric acid; this is now shown to be true of cellulose from the *Pezizaceæ* (*Botrytis* and *Polyporus*). The same result is obtained if the residue obtained after the fungi have been freed from fat and boiled first with dilute sulphuric acid and then with dilute caustic soda is used, instead of the prepared cellulose.

It is also shown that, just as in the case of chitin, acetic acid is formed in addition to glucosamine; moreover, the above-mentioned residues behave like chitin when fused for an hour with caustic potash at a temperature not exceeding 180°; they yield acetic acid and a substance resembling chitosan. Various species of *Polyporus* furnish, in addition, a cellulose-like substance, insoluble in water, and yielding glucose when hydrolysed. No such product was obtained from *Boletus*, *Agaricus*, or *Morchella*, but the cellulose from the first two yields glucose when hydrolysed, and must therefore contain, in addition to chitin, a substance, possibly a hemicellulose, which yields glucose when hydrolysed, but is destroyed in the potash fusion.

C. F. B.

Complex Metallic Bases. By Nicolai S. Kurnakoff (*J. pr. Chem.*, 1894, [2], **50**, 481—507).—The salient points in this paper have already been published (Abstr., 1894, i, 273). A. G. B.

A New Series of Sulphur Derivatives of Aliphatic Amines. By AUGUST MICHAELIS and K. LUXEMBOURG (*Ber.*, 1895, **28**, 165—167). —When sulphur chloride is mixed with secondary amines in cooled ethereal solution, the following reaction occurs:—$S_2Cl_2 + 4NHR_2 = S_2(NR_2)_2 + 2NHR_2,HCl$. The *dithiodiamines* formed are decomposed by acids into the amine, sulphur, and sulphurous anhydride. *Dithiodimethylamine*, $S_2(NMe_2)_2$, is a reddish-yellow liquid, boiling at 82—83° under 22 mm. pressure, at 170—180°, and with slight decomposition, under atmospheric pressure. *Dithiodiethylamine*, $S_2(NEt_2)_2$, is a pale yellow liquid, boiling at 137—138° under 29 mm. pressure, and decomposing when distilled under atmospheric pressure. *Dithiodipiperidine*, $S_2(C_5NH_{10})_2$, forms white crystals melting at 64°.

Sulphur chloride also reacts with primary amines, but the products have not yet been carefully studied. C. F. B.

Choline. By ERNST SCHMIDT (*Zeit. physiol. Chem.*, 1895, **20**, 364). —Gulewitsch (this vol., i, 196) finds that Gram's statement concerning the ready conversion of choline into neurine by hydrochloric and lactic acid is incorrect. The present paper shows that the author previously pointed out Gram's error. W. D. H.

So-called Stereochemistry of Nitrogen. By ADOLPH CLAUS (*J. pr. Chem.*, 1894, [2], **50**, 567—576).—The author takes exception to the statements which Van't Hoff makes, in the recently published second edition of his book on "*die Lagerung der Atome in Raum*," concerning the isomerism of the oximes. He (the author) has brought forward many instances of oximes which, although fulfilling the conditions laid down by Van't Hoff, do not show isomerism, and devotes this paper to a review of his position. A. G. B.

Thiosemicarbazide. By MARTIN FREUND (*Ber.*, 1895, **28**, 306; compare *Ber.*, 1895, **28**, 77).—The melting point of thiosemicarbazide is really 181—183°, and not 215—218°, as previously stated. A. H.

Polymeric Modifications of Propaldehyde. Parapropaldehyde, and Metapropaldehyde. By WILLIAM R. ORNDORFF and Miss L. L. BALCOM (*Amer. Chem. J.*, 1894, **16**, 645—650; compare Abstr., 1890, 955; 1894, i, 168).—*Parapropaldehyde*, obtained from pure propaldehyde by the polymerising action of hydrogen chloride, solidifies completely at −20° to a mass of needle-shaped crystals, and boils at 169—170° (uncorr.), being converted into propaldehyde. It has a sp. gr. of 0·9549 at 0°/4°, is only slightly soluble in water, dissolves readily in ether and in alcohol, and closely resembles paraldehyde in odour and properties. It does not react with hydroxylamine or with a solution of magenta which has been decolorised with sulphurous anhydride, and its molecular weight, as determined by its effect in lowering the melting point of phenol, corresponds with the formula $C_9H_{18}O_3$ (compare Reformatsky, *J. Russ. Chem. Soc.*, **22**, 197).

The method of preparation of metapropaldehyde has been already described (*loc. cit.*). It closely resembles metaldehyde in its properties, and does not react with hydroxylamine or affect a solution of

magenta decolorised by sulphurous anhydride, and consequently does not contain a COH group. Its molecular weight, determined in the same way as that of parapropaldehyde, accords also with the formula $C_9H_{18}O_3$. On being kept for some time, it appears to be partly converted into a tetrapropaldehyde, $(C_3H_6O)_4$.

As neither parapropaldehyde nor metapropaldehyde contains a COH group; as their molecules are of equal weight, and as they both are readily converted into the simple aldehyde by the action of the same reagents, the author suggests that the oxygen atoms play the parts of connecting links, and that the two aldehydes are stereoisomerides. Parapropaldehyde, being the more stable, is probably the trans-variety, and metapropaldehyde the cis-variety.

G. T. M.

Oxidation of Aliphatic Aldehydes and Ketones by Nitric acid. By Robert Behrend and Heinrich Tryller (*Annalen*, 1894, **283**, 209—245; compare Abstr., 1893, i, 303, and 1894, i, 108).—Hydroxyisonitrosoacetone nitrite (*loc. cit.*), obtained by oxidising acetone with nitric acid, is to be regarded as *acetylmethylnitrolic acid*, $COMe{\cdot}C(NOH){\cdot}NO_2$; it crystallises from ether in transparent plates, which melt at 55—62° with evolution of gas. In addition to the products already mentioned (*loc. cit.*), the yellow oil, obtained by the action of nitric acid on acetone, yields pyruvic acid when boiled with water. When the oil is heated, it decomposes and becomes viscous, yielding, on treatment with hydroxylamine hydrochloride, an *oxime*, $C_6H_8N_4O_4$, which melts and decomposes at 139—140°; nitric acid converts this substance into a *compound* of the formula $C_6H_6N_4O_5$.

The fact that acetone is acted on by cold nitric acid only when the latter contains nitrous acid, appears to depend on the initial production of isonitrosoacetone, which is then in part converted into acetylmethylnitrolic acid, oxidation occurring at the same time. This explanation is confirmed by the observation that action may be set up in a mixture of acetone and pure nitric acid by introducing a small quantity of isonitrosoacetone; moreover, when mixed with nitric acid of sp. gr. 1·4, isonitrosoacetone is converted into acetylmethylnitrolic acid.

When methyl ethyl ketone is acted on by nitric acid to which a little red fuming acid has been added, formic and acetic acids are formed, together with a small quantity of hydrogen cyanide and ammonia; the other products are ethylnitrolic acid and dinitroethane, the former arising in consequence of the initial formation of isonitrosomethyl ethyl ketone, whilst the latter results from the action of nitric acid on ethylnitrolic acid.

When nitrous acid acts on acetone, acetylmethylnitrolic acid is formed. In the case of methyl ethyl ketone, the products are the isonitroso-derivative and ethylnitrolic acid. M. O. F.

Action of Ethylic Chlorocarbonate on the Sodium Derivative of Acetone. By Paul C. Freer (*Annalen*, 1894, **283**, 380—391, and *Amer. Chem. J.*, 1895, **17**, 1—18; compare Freer and Higley, Abstr., 1891, 1182).—When ethylic chlorocarbonate acts on sodacetone, a

mixture of sodium chloride and carbonate separates, and a highly refractive oil, which boils at 129—130°, is formed; hydrolysis of this substance with barium hydroxide or with dilute hydrochloric acid gives rise to carbonic anhydride, ethylic and isopropylic alcohols, and acetone. On effecting this decomposition quantitatively, results are obtained, which, in conjunction with analyses and vapour-density determinations, give support to the view that the chief product of the action of ethylic chlorocarbonate on sodacetone is *ethylic isoacetonecarbonate*, $CH_2{:}CMe{\cdot}O{\cdot}COOEt$ (*loc. cit.*).

A *substance*, $C_9H_{14}O_3$, is formed at the same time, and can be separated on account of its higher boiling point. It has an odour suggestive of that of mesitylic oxide, and is indifferent towards phenylhydrazine; it boils at 114° under a pressure of 30 mm. The constitution is probably represented by the expression

$$CMe_2{:}CH{\cdot}C(:CH_2){\cdot}O{\cdot}COOEt.$$

Ethylic isoacetonecarbonate, when treated with phosphorus pentachloride, yields a mixture of β-chloropropylene and ethylic chlorocarbonate with a small quantity of diethylic carbonate.

M. O. F.

Ethereal Salts from Active Amylic Alcohol. By PHILLIPE A. GUYE and L. CHAVANNE (*Compt. rend.*, 1894, **119**, 906—909).—The authors have prepared a number of salts from active primary amylic alcohol and the normal acids of the acetic series, and have determined their rotatory powers, with the following results.

	B. p. under 727 mm.	Sp. gr. at 21—24°.	Specific rotatory power $[\alpha]_D$.	Product of asymmetry $P \times 10^6$.
Amylic formate...	120—122°	0·882	+2·01	332
„ acetate...	138—139	0·872	+2·53	**374**
„ propionate	156—158	0·869	**+2·77**	373
„ butyrate..	173—176	0·862	+2·69	351
„ valerate..	195—197	0·860	+2·52	321
„ caproate..	212—214	0·859	+2·40	289
„ heptylate .	232—235	0·861	+2·21	258
„ caprylate .	250—253	0·860	+2·10	229
„ nonylate..	262—265	0·861	+1·95	204
„ laurate...	305—308	0·859	+1·56	144
„ palmitate .	9·5° m. p.	0·854	+1·45	93·5
„ stearate ..	20–21° m. p.	0·855	+1·27	76·7

The value of $[\alpha]_D$ passes through a maximum corresponding with amylic propionate, whilst the product of asymmetry passes through a maximum corresponding with amylic acetate. The simplified formula adopted by the authors for the product of asymmetry, whilst it indicates the occurrence of a maximum, is not sufficient to exactly determine its position *à priori*.

In the preparation of the salts, phosphoric anhydride, as recommended by Young and Thomas (Trans., 1893, 1191), was found to be the only convenient means of removing the excess of amylic alcohol.

Amylic alcohol, obtained by hydrolysing the formate and the palmitate, has the same optical activity as the original alcohol. This fact disposes of (1) the objection of Frankland and Macgregor (Trans., 1893, 1410—1418) that the amylic alcohol employed may be a mixture of two alcohols that etherify at different rates with acids so different in boiling point as formic and palmitic acids, the occurrence of a maximum being then fortuitous; and (2) the objection of Van't Hoff, that partial racemisation may take place during fractional distillation. C. H. B.

Ethylic Mercuridiazoacetate. By EDUARD BUCHNER (*Ber.*, 1895, **28**, 215—221).—This substance, $Hg[C(:N_2)\cdot COOEt]_2$, is obtained by dissolving mercuric oxide in cooled ethylic diazoacetate,

$$N_2:CH\cdot COOEt;$$

it forms yellow, rhombic crystals, $a : b : c = 0{\cdot}4546 : 1 : 0{\cdot}72527$, and melts and decomposes at 104°. The corresponding *methylic* salt melts, and decomposes slightly, at 123°. These compounds are slightly explosive and are readily decomposed. The action of water on them has been studied in some detail; at the ordinary temperature it converts the methylic salt into mercury, nitrogen, methylic alcohol, oxalic acid, and glycolic acid. C. F. B.

Active Amylacetic acid and its Derivatives. By IDA WELT (*Compt. rend.*, 1894, **119**, 855—858).—*Ethylic amylacetoacetate*, specific rotatory power at 20°, $[\alpha]_D = +7{\cdot}71$.

Amylacetic acid, boiling at 221°, sp. gr. at 20° = 0·9149; at 54° = 0·8902. Specific rotatory power at 20°, $[\alpha]_D = +8{\cdot}44°$; at 54°, $[\alpha]_D = +7{\cdot}64°$.

Methylic amylacetate, sp. gr. at 25° = 0·8764, and at 61° = 0·8449. Specific rotatory power at 25°, $[\alpha]_D = +6{\cdot}71$, and at 75°, $[\alpha]_D = +5{\cdot}92$. *Ethylic amylacetate*, sp. gr. at 21° = 0·8644, and at 72° = 0·8250. Specific rotatory power at 21°, $[\alpha]_D = +6{\cdot}66$, and at 72°, $[\alpha]_D = +5{\cdot}87$.

Methyl hexyl ketone, $COMe\cdot CH_2\cdot C_5H_{11}$, is obtained by the action of potassium hydroxide on ethylic amylacetoacetate, and boils at 167—168°; sp. gr. at 19° = 0·8174, and at 57°, 0·7893; specific rotatory power at 21°, $[\alpha]_D = +5{\cdot}06$, and at 57°, $[\alpha]_D = +4{\cdot}41$. The other optically active products formed at the same time are very viscous liquids, boiling at 310—330° and 330—370° respectively; the latter seems to be mesitylic oxide.

Methylhexylcarbinol, $OH\cdot CHMe\cdot CH_2\cdot C_5H_{11}$, obtained by the action of sodium on an alcoholic solution of the ketone, boils at 167—170°; sp. gr. at 21° = 0·8174, specific rotatory power at 24°, $[\alpha]_D = +4{\cdot}69$.

In the case of methylic and ethylic amylacetates, the value of the product of asymmetry, like the rotatory power, decreases, and hence it follows that in this series there is no ethereal salt showing a maximum rotatory power, even the first term being already on the descending branch of the curve. (Compare this vol., ii, 97.)

C. H. B.

Intramolecular Changes in Unsaturated Acids. By RUDOLPH FITTIG (*Annalen*, 1894, **283**, 47—65; compare Abstr., 1893, i, 189).—This paper embodies the experimental results described in the following communications. As already stated (*loc. cit.*), $\beta\gamma$-unsaturated acids are changed by boiling aqueous soda into the isomeric $\alpha\beta$-acids, which, unlike the former, are not converted into lactones by dilute sulphuric acid; this difference in behaviour affords a ready means of separating the isomerides. The method, however, is not applicable to aromatic unsaturated acids, owing to the formation of acid bye-products during the conversion of the $\beta\gamma$-acids into the isomeric lactones; moreover, the $\alpha\beta$-acids yield lactones under the influence of dilute sulphuric acid.

The conversion of $\beta\gamma$-unsaturated acids into the $\alpha\beta$-isomerides is attended with the formation of β-hydroxy acids; the γ-hydroxy-acids are never formed, nor can they be obtained by the action of boiling aqueous soda on the β-acid. The production of a mixture of $\alpha\beta$- and $\beta\gamma$-unsaturated acids when the β-hydroxy-acids are treated with soda, finds a parallel in the behaviour of the β-bromo-acids. These, in general, are converted by boiling water into a mixture of $\alpha\beta$- and $\beta\gamma$-unsaturated acids, with a preponderating amount of β-hydroxy-acid; in the case of phenyl-β-bromovaleric acid, however, the $\beta\gamma$-acid is not formed. M. O. F.

Intramolecular Change in $\beta\gamma$-Pentenic (Ethylidenepropionic) acid. Experiments with $\gamma\delta$-Pentenic acid. By RUDOLPH FITTIG and JOHN G. SPENZER (*Annalen*, 1894, **283**, 66—79 and 79—81).—When the sodium salt of $\beta\gamma$-pentenic acid is boiled in aqueous solution with 10 per cent. soda (9 mols.) for 10—20 hours in a copper flask, it is converted into sodium propylideneacetate (compare Ott, Abstr., 1891, 1453). The barium salt contains $4H_2O$, losing $2H_2O$ with great readiness; the calcium salt, with $4H_2O$, forms flat, nacreous prisms. Bromine converts the acid into $\alpha\beta$-dibromovaleric acid, β-bromovaleric acid being formed by the action of hydrogen bromide.

β-Hydroxyvaleric acid is produced during the conversion of ethylidenepropionic into propylideneacetic acid. It is a colourless syrup which remains liquid at $-18°$. The *calcium* salt contains $1H_2O$; it becomes anhydrous at 175°, and melts at 180°. The *barium* salt forms monosymmetric plates which contain $1H_2O$ and melt at 105°; the *silver* salt is also crystalline. When the aqueous solution of the acid is boiled for 30 hours with soda, rather more than one half is unattacked; the remainder, however, is converted into a mixture of ethylidenepropionic and propylideneacetic acids. These acids are also produced when β-hydroxyvaleric acid is submitted to dry distillation.

Allylmalonic and allylacetic acids are quite indifferent towards alkali. M. O. F.

Pentenic Acids from the Interaction of Propaldehyde and Malonic acid. By RUDOLPH FITTIG and JOHN E. MACKENZIE (*Annalen*, 1894, **283**, 82—100; compare preceding abstract, and

A. Viefhaus, Abstr., 1893, i, 392).—The conclusion arrived at by Viefhaus (*loc. cit.*), respecting the composition of the acid mixture obtained by heating propaldehyde with malonic and acetic acids, is confirmed.

Boiling water converts β-bromovaleric acid into a mixture of β-hydroxyvaleric acid (56 per cent.), propylideneacetic (11 per cent.), and ethylidenepropionic (10 per cent.) acids; a small quantity of butylene is also produced.

Ethylidenepropionic acid yields $\beta\gamma$-dibromovaleric acid when acted on by bromine; this crystallises in transparent prisms which melt at 65—65·5° (compare Fittig and Fränkel, Abstr., 1890, 585). Hydrogen bromide converts it into a mixture of β- and γ-bromovaleric acids, which, when boiled with water, yields ethylidenepropionic, propylideneacetic, and β-hydroxyvaleric acids, mixed with valerolactone (50 per cent.). M. O. F.

Crystalline Form of Bromo- and Dibromo-valeric acids. By Rudolph Fittig (*Annalen*, 1894, **283**, 100—104).—β-Bromovaleric acid forms monosymmetric crystals; $a : b : c = 1{\cdot}4688 : 1 : 0{\cdot}4900$. $\beta = 79° 58' 45''$.

$\alpha\beta$-, $\beta\gamma$-, and $\gamma\delta$-dibromovaleric acids also form crystals belonging to the monosymmetric system, and having the following ratios respectively.

$a : b : c = 1{\cdot}2016 : 1 : 0{\cdot}4808.$	$\beta = 88° 48'$
$a : b : c = 0{\cdot}9509 : 1 : 0{\cdot}8781.$	$\beta = 82 \ 20$
$a : b : c = 5{\cdot}5159 : 1 : \ ?$	$\beta = 77 \ 10$

M. O. F.

Intramolecular Change in Angelic and Tiglic acids. By Rudolph Fittig (*Annalen*, 1894, **283**, 105—109).—The separation of angelic and tiglic acids by means of the calcium salts is almost quantitative; it is therefore possible to study their behaviour towards boiling aqueous soda.

When angelic acid (10 grams) is heated with soda (40 grams), dissolved in water (160 grams) for 20 hours in a reflux apparatus, tiglic acid (6·3 grams) is formed. The yield is influenced by the temperature maintained, and therefore depends on the concentration of the alkali employed. Thus, when angelic acid is heated with water (15 parts) for 20 hours at 120°, one-half its weight of tiglic acid is produced.

Tiglic acid undergoes no change when heated for 20 hours with a 20 per cent. solution of soda. M. O. F.

Oxidation of Tiglic and Angelic acids. By Rudolph Fittig and Max Penschuck (*Annalen*, 1894, **283**, 109—117; compare I. Kondakoff, Abstr., 1892, 1304).—*Tigliceric acid*, $C_5H_8(OH)_2O_2$, is obtained by the oxidation of tiglic acid in alkaline solution with potassium permanganate. It melts at 88°, and forms crystals belonging to the monosymmetric system; $a : b : c = 1{\cdot}0665 : 1 : 0{\cdot}7903$. $\beta = 73° 26'$. The *barium*, *calcium*, and *silver* salts are very soluble in water; the *zinc* salt dissolves more readily in cold water than in hot.

Angliceric acid is obtained in a similar manner from angelic acid;

it melts at 110—111°. The *calcium* and *zinc* salts are readily soluble in water.

Neither of these acids yields a hydroxy-lactone under the influence of hydrochloric acid. M. O. F.

Intramolecular Change in $\beta\gamma$-Hexenic (Hydrosorbic) acid. By Rudolph Fittig and Charles F. Baker (*Annalen*, 1894, **283**, 117—128).—*$\alpha\beta$-Hexenic acid*, $CH_2Me{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$, is formed when hydrosorbic acid is heated with a 20 per cent. solution of soda for 20—50 hours. It melts at 32·7—33·1°, and boils at 216—217°. The *calcium* salt, with $3H_2O$, forms white plates; the *barium* salt contains $1\frac{1}{2}H_2O$. The *silver* salt forms white needles, the *cadmium* salt contains $2H_2O$, and the *zinc* salt with $2\frac{1}{2}H_2O$ crystallises in silky needles. Bromine converts the acid into *$\alpha\beta$-dibromocaproic acid*, which melts at 70·5—71·5°, and differs from the isomeride obtained from sorbic acid and hydrogen bromide. *β-Bromocaproic acid* is obtained by the action of hydrogen bromide on $\alpha\beta$-hexenic acid; it is insoluble in water, and melts at 34·5—35°. When boiled for two hours with water, carbonic anhydride is eliminated, and a small quantity of amylene is formed; rather more than half the acid, however, is converted into *β-hydroxycaproic acid*, a colourless syrup which dissolves readily in water, and is not volatile in a current of steam. The *barium* salt crystallises in white plates containing $1H_2O$, and the *calcium* salt contains $\frac{1}{2}H_2O$; the *silver* salt forms white needles.

$\alpha\beta$-Hexenic acid yields about one-fourth of its weight of β-hydroxycaproic acid when boiled with 10 per cent. aqueous soda, the remainder undergoing no change. This action is reversible, β-hydroxycaproic acid yielding 30 per cent. of $\alpha\beta$-hexenic acid when treated with boiling aqueous soda. M. O. F.

Intramolecular Change in $\beta\gamma$-Isoheptenic acid. By Rudolph Fittig and Julius Feurer (*Annalen*, 1894, **283**, 129—148).—*$\alpha\beta$-Isoheptenic acid*, $CHMe_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$, is obtained by heating $\beta\gamma$-isoheptenic acid with 10 per cent. aqueous soda for 30 hours; it melts at 16·5°, and boils at 227—228°. The *calcium* salt with $4H_2O$ forms characteristic aggregates of needles; the *barium* salt resembles it, and contains $7\frac{1}{2}H_2O$. The *silver* salt crystallises in lustrous plates, and is not altered by light. *$\alpha\beta$-Dibromisoheptoic acid*, which melts at 116—117°, forms crystals belonging to the monosymmetric system; $a : b : c = 0{\cdot}732 : 1 : 0{\cdot}641$. $\beta = 58°\ 0'\ 9''$. *β-Bromisoheptoic acid* is obtained by the action of hydrogen bromide on $\alpha\beta$-isoheptenic acid; it melts at 26—27°, and dissolves very readily in organic solvents. Boiling water converts it into a mixture of hexylene, $\alpha\beta$- and $\beta\gamma$-isoheptenic acids, and *β-hydroxyisoheptoic acid*, the latter being also obtained by the action of boiling aqueous soda on $\beta\gamma$-isoheptenic acid; it forms small, lustrous plates, and melts at 64·5°. The *barium* salt contains $2H_2O$, and the *calcium* salt $1\frac{1}{2}H_2O$; the *silver* salt is indifferent towards light. When β-hydroxyisoheptoic acid is submitted to dry distillation, nearly one-half passes over unchanged, whilst the remainder is converted into $\alpha\beta$-isoheptenic acid with a small quantity of the $\beta\gamma$-acid. These

acids are also formed when the hydroxy-acid is heated with 10 per cent. aqueous soda for 30 hours, 75 per cent. remaining unaltered.

Boiling aqueous soda converts $\alpha\beta$-isoheptenic acid into a mixture of β-hydroxyheptoic and $\beta\gamma$-isoheptenic acids. M. O. F.

Oxidation Products of $\beta\gamma$- and $\alpha\beta$-Isoheptenic acids. By RUDOLPH FITTIG and ALFRED SILBERSTEIN (*Annalen*, 1894, **283**, 269—279).—*Hydroxyisoheptolactone*,

$$CHMe_2\cdot CH<\begin{matrix}CH(OH)\cdot CH_2\\ O\text{———}\end{matrix}>CO,$$

is obtained by oxidising $\beta\gamma$-isoheptenic acid with potassium permanganate. It melts at 112°, and forms crystals belonging to the monosymmetric system; $a : b : c = 2{\cdot}1494 : 1 : 1{\cdot}2600$. $\beta = 78°\ 3'$. When the lactone is heated with hot aqueous barium hydroxide, the *barium* salt of $\beta\gamma$-dihydroxyheptoic acid is formed; the *calcium* salt contains $1H_2O$, and the silver salt rapidly darkens on exposure to light.

Isoheptenolactone, $CHMe_2\cdot C<\begin{matrix}CH\cdot CH_2\\ O\text{———}\end{matrix}>CO$, is formed on distilling hydroxyisoheptolactone; it is a colourless oil which boils at 225—230°.

δ-Dimethyllevulinic acid, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$, is obtained by the action of hot aqueous alkalis on isoheptenolactone; it crystallises in long needles, and melts at 41°. The *barium* salt is anhydrous.

$\alpha\beta$-Dihydroxyisoheptoic acid,

$$CHMe_2\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot COOH,$$

is obtained by oxidising $\alpha\beta$-isoheptenic acid. It crystallises in small needles, and melts at 114°. The *calcium* salt contains $3H_2O$, and the *barium* salt $1H_2O$; the *silver* salt slowly becomes coloured when exposed to light. The acid does not form a lactone, and remains unchanged when heated with 10 per cent. aqueous soda for 20 hours, resembling, in this respect, the $\beta\gamma$-isomeride. M. O. F.

Intramolecular Change in $\beta\gamma$-Isoctenic acid. By RUDOLPH FITTIG and SYLVIAN WEIL (*Annalen*, 1894, **283**, 279—291).—The *anhydride* of isobutylcitraconic acid is produced on distilling isobutylparaconic acid; the *acid* itself, $C_9H_{14}O_4$, melts at 75—80°, and forms a *barium* salt which is more soluble in cold water than in hot.

$\beta\gamma$-Isoctenic acid is also formed when isobutylparaconic acid is distilled, and on treatment with a hot, 10 per cent. solution of soda for 30 hours, it is converted into *$\alpha\beta$-isoctenic acid*, which melts at 3° and boils at 239—240°; this action is reversible. The *calcium* salt contains $1H_2O$, and the *barium* salt is anhydrous; the *silver* salt becomes yellow on exposure to light.

$\alpha\beta$-Dibromisoctoic acid crystallises in needles which melt at 58—59°. *β-Bromisoctoic acid* is obtained by the action of hydrogen bromide on $\alpha\beta$-isoctenic acid. It is a yellowish oil, and when boiled with water yields a mixture of $\alpha\beta$- and $\beta\gamma$-isoctenic acids with *β-hydroxyisoctoic acid*, which is also obtained by heating $\beta\gamma$-isoctenic

acid with aqueous soda. It crystallises in silky needles, and melts at 36—37°. The *barium* and *calcium* salts contain $1H_2O$; the *silver* salt is not changed by exposure to light. M. O. F.

Oxidation Products of $\beta\gamma$- and $\alpha\beta$-Isoctenic acids. By Rudolph Fittig and François de Vos (*Annalen*, 1894, **283**, 291—297).—*Hydroxyisoctolactone*, $CHMe_2\cdot CH_2\cdot CH<\overset{CH(OH)\cdot CH_2}{O\text{———}\cdot\text{———}}>CO$, is produced when $\beta\gamma$-isoctenic acid is oxidised with potassium permanganate; it crystallises in needles, and melts at 33—34°. Hot aqueous alkalis convert the lactone into salts of $\beta\gamma$-dihydroxyisoctoic acid; the *barium* and *calcium* salts are crystalline, and do not contain water; the *silver* salt is also crystalline. When the lactone is distilled, an unsaturated lactone is formed, and this is converted by alkalis into *isopropyllevulinic acid*, which crystallises in colourless needles, and melts at 47°. The *barium* salt is anhydrous, and the *calcium* salt contains $3H_2O$; the *silver* salt forms colourless crystals.

$\alpha\beta$-Dihydroxyisoctoic acid,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot COOH,$$

is obtanied by oxidising $\alpha\beta$-isoctenic acid with potassium permanganate; it does not give rise to a lactone, and is quite indifferent towards 10 per cent. aqueous soda. The *barium* and *calcium* salts are anhydrous; the *silver* salt crystallises from hot water.

M. O. F.

Stearoxylic acid and Behenoxylic acid. By A. Spieckermann (*Ber.*, 1895, **28**, 276—279).—Stearoxylic acid reacts with hydroxylamine to form *diketoximestearic acid*,

$$Me\cdot[CH_2]_7\cdot C(N\cdot OH)\cdot C(N\cdot OH)\cdot[CH_2]_7\cdot COOH,$$

which crystallises in white, microscopic needles, melting at 153—154°. *Diketoximebehenic acid*,

$$Me\cdot[CH_2]_7\cdot C(N\cdot OH)\cdot C(N\cdot OH)\cdot[CH_2]_{11}\cdot COOH,$$

is obtained in a similar manner from behenoxylic acid, and crystallises in matted, white needles which melt at 144—145°. When only about 1 mol. of hydroxylamine is used, the ketoximebehenic acid is accompanied by behenic acid and *ketoximeketobehenic acid*, which forms microscopic needles melting indefinitely at 83—88°.

Stearoxylic acid is therefore 9 : 10-diketostearic acid, whilst behenoxylic acid is 13 : 14-diketobehenic acid. A. H.

Electrosyntheses by the Direct Union of Anions of Weak Organic Acids. By J. B. Weems (*Amer. Chem. J.*, 1894, **16**, 569—588).—The author has investigated the behaviour of such oxidising agents as hydrogen peroxide, potassium permanganate, and chromic acid on ethylic malonate, ethylic methanetricarboxylate, and acetylacetone, and finds that the same products are not obtained as when those substances are electrolysed. The formation of the new compounds by electrolysis is best explained as the result of the direct union of the anions. This union takes place very readily during the electrolysis of sodium compounds of derivatives of ethylic malonate. Ethylic dimethylethanetetracarboxylate and diethylethanetetracarb-

oxylate are thus obtained from ethylic methylmalonate and ethylmalonate, but in yield smaller than from ethylic malonate and ethylic methanetricarboxylate. No evidence of a pairing of anions was obtained during the electrolysis of ethylic benzoylmalonate and acetylmalonate. Compounds such as ethylic acetoacetate and slightly impure acetylacetone gave, on electrolysis, distinct evidence of the pairing of anions, but no such synthetical products were obtained from ethylic acetonedicarboxylate and acetylbenzoylmethane, and the reaction must not therefore be regarded as a typical one. The formation of bis-phenylmethylpyrazalone in the electrolysis of phenylmethylpyrazalone may be partly an electrolysis of this type, or may be due entirely to oxidation.

The electrolysis of acid amides, such as acetamide, benzamide, succinimide, and phthalimide, or of their sodium or mercury derivatives, yields the original amides or imides without any pairing of anions. G. T. M.

Trimethylsuccinic acid and the Symmetrical Dimethylglutaric acids. By KARL AUWERS (*Ber.*, 1895, **28**, 263—270).—According to Zelinsky (Abstr., 1891, 669), two isomeric trimethylsuccinic acids are formed by the hydrolysis of the product of the action of ethylic α-bromisobutyrate on ethylic α-cyanopropionate. Since the accepted stereochemical theory only admits the possibility of one acid of this constitution, and as the statements of different investigators with regard to these acids are not in complete agreement, the author has reinvestigated the matter. He has found that trimethylsuccinic acid only exists in one form, and that symmetrical dimethylglutaric acid exists in two stereoisomeric forms. The acid usually described as symmetrical dimethylglutaric acid, and that supposed by Zelinsky to be a second trimethylsuccinic acid, are both mixtures of the two isomeric dimethylglutaric acids.

Trimethylsuccinic acid was prepared by Zelinsky's method, by the oxidation of camphoric acid (Abstr., 1894, i, 46), by the dry distillation of camphoronic acid (Abstr., 1894, i, 141; Helle, *Inaug. Diss.*, Bonn, 1893, 21), and by the action of ethylic α-bromisobutyrate on ethylic sodiomethylmalonate in solution in xylene and in alcohol (Abstr., 1891, 828; Helle). The pure acid obtained by each of these methods melts at 147—148°, but the melting point varies a little with the rate at which the acid is heated. The numbers given by previous investigators vary from 131° to 141°. At 152—153° the acid loses water and forms the anhydride, which boils at 227° and melts at 31°; 100 parts of water dissolve 9·57 of the acid at 15°. The electrical conductivity $k = 0{\cdot}0304$. The *barium* and *zinc* salts are crystalline. The following derivatives have been prepared. The *anilic acid*, melting at 134—135°, the *anil*, melting at 129°, the *paratolil*, melting at 117°, and the *β-naphthil*, of melting point 148°, crystallise in needles, whilst the *paratolilic acid*, which melts at 126°, forms tablets, and the *β-naphthilic acid*, melting at 153°, crystallises in prisms.

Symmetrical dimethylglutaric acid obtained from ethylic sodio-α-cyanopropionate and methylenic iodide (Abstr., 1890, 132) from the

latter and ethylic sodiomethylmalonate (Abstr., 1890, 1099) from ethylic α-bromisobutyrate and ethylic sodiomethylmalonate (Abstr., 1890, 743, 1098; 1891, 1015; 1894, i, 72), and by the methylation of ethylic dicarboxyglutarate (Abstr., 1891, 178) is a mixture in nearly equal proportions of two stereoisomeric acids. The acid obtained by Zelinsky, and supposed by him to be a new trimethylsuccinic acid, on the other hand, contains much more of the maleïnoid than of the fumaroïd acid. The two can readily be separated by means of the calcium salts, or by the action of acetic chloride.

The *fumaroïd acid*, which has not previously been described, crystallises from hot water in compact flat monosymmetric needles melting at 140—141°. One hundred parts of water dissolve 4·4 of the acid at 17°; 5·6 at 25°. The acid is not volatile with steam, even from solutions made strongly acid with sulphuric acid, has an electrical conductivity $k = 0{\cdot}00593$, and is optically inactive. It may be distilled under reduced pressure without undergoing any change, and small quantities may be distilled under the ordinary pressure, but when slowly distilled in the air, it loses water, and forms the *anhydride* melting at 94—95°, which is given by both of the acids. Hydrochloric acid at 190—200° partially transforms the acid into the stereoisomeric form, a mixture of about equal parts of the two forms being produced. Boiling acetic chloride is without action, but at 100° produces the anhydride mentioned above.

The acid melting at 127—128°, which has been described by Zelinsky, is the maleïnoid form; 100 parts of water dissolve 4·1 of the acid at 15°; 4·9 at 25°. When distilled at a low pressure, the acid is not decomposed, but is partially converted into the isomeride; at 200 mm. it is largely converted into the anhydride. Acetic chloride converts it in the cold into the anhydride, whilst hydrochloric acid at a high temperature partially converts it into the isomeride. The anhydride boils at 272°, and solidifies to monosymmetric crystals. The *imide* obtained from both of the acids crystallises in needles melting at 173—174°. The *anilic acid*, melting at 157°; the *anil*, at 208—209°; the *paratolilic acid*, at 179°; the *paratolil*, at 233°; the *β-naphthil*, at 231—232°; and the *α-naphthilic acid*, at 155°, all crystallise in needles, whilst the *β-naphthilic acid* forms flat prisms melting at 151°, and the *α-naphthil* crystallises in plates melting at 199°. A mixture of equal parts of these two acids melts at 104·5°, and has been hitherto mistaken for a single acid (Zelinsky, Bischoff, Auwers); 100 parts of water dissolve 8·5 of the mixed acids at 17°. As already mentioned, the acid melting at 100—101°, which was described by Zelinsky as trimethylsuccinic acid, is a mixture of the two dimethylglutaric acids, the maleïnoid form being present in greater proportion. A. H.

Secondary Ethereal Acidyltartrates. By P. Freundler (*Bull. Soc. Chim.*, 1894, [3], **11**, 366—374).—With two exceptions, these are all liquids, and have somewhat lower boiling points than the corresponding normal compounds (compare this vol., i, 174).

Isopropylic diacetyltartrate crystallises in prisms, and melts at 33°;

the rotatory power in alcoholic solution at 20° is $[\alpha]_D = +5{\cdot}9°$. The *isobutylic* salt boils under 12 mm. pressure at 196—197°; the sp. gr. = 1·096 at 16·5°. The sp. rotatory power of the liquid at 18·5° is $[\alpha]_D = +17°$; of the alcoholic solution, $[\alpha]_D = +11{\cdot}8°$.

Isobutylic dipropionyltartrate boils under 15 mm. pressure at 207—208°; the sp. gr. = 1·073 at 16·5°. The sp. rotatory power at 19° of the liquid is $[\alpha]_D = +11{\cdot}4°$; of the alcoholic solution, $[\alpha]_D = +10{\cdot}2°$. The *dibutyryltartrate* boils under 20 mm. pressure at 221—223°; the sp. gr. = 1·050 at 16°. The sp. rotatory power at 19° of the liquid is $[\alpha]_D = +8{\cdot}5°$; of the alcoholic solution, $[\alpha]_D = +8{\cdot}1°$. The *divaleryltartrate* decomposes when boiled; the sp. gr. = 1·032 at 18·5°; the sp. rotatory power of the liquid is $[\alpha]_D = +7{\cdot}4°$; of the alcoholic solution, $[\alpha]_D = +7{\cdot}7°$. The *dicaproyltartrate* has a sp. gr. = 1·013 at 13°. The sp. rotatory power at 16° is $[\alpha]_D = +6{\cdot}0°$, that of the alcoholic solution, $[\alpha]_D = +5{\cdot}5°$.

Methylic diisobutyryltartrate crystallises in prisms, and melts at 45°; the sp. rotatory power of the alcoholic solution at 17° is $[\alpha]_D = -13{\cdot}4°$. The *ethylic* salt has a sp. gr. = 1·095 at 17°. The sp. rotatory power at 17·5° is $[\alpha]_D = -1{\cdot}5°$; that of the alcoholic solution, $[\alpha]_D = +1{\cdot}4°$. The *propylic* salt has a sp. gr. = 1·066 at 16°. The sp. rotatory power at 18° is $[\alpha]_D = +2{\cdot}2°$; that of the alcoholic solution, $[\alpha]_D = +4{\cdot}7°$. The *isobutylic* salt has a sp. gr. = 1·048 at 16·5°. The sp. rotatory power at 14° is $[\alpha]_D = +8{\cdot}4°$; that of the alcoholic solution, $[\alpha]_D = +10{\cdot}1°$.

Methylic diisovaleryltartrate is a liquid of sp. gr. 1·107 at 16·5°; the sp. rotatory power at 14·5° is −13·9°; that of the alcoholic solution, $[\alpha]_D = -9{\cdot}4°$. The *ethylic* salt has a sp. gr. = 1·067 at 17·5°. The sp. rotatory power at 16° is $[\alpha]_D = -1{\cdot}4°$; that of the alcoholic solution, $[\alpha]_D = +0{\cdot}5°$. The *propylic* salt has a sp. gr. = 1·049 at 18·5°. The sp. rotatory power at 16° is $[\alpha]_D = +0{\cdot}7°$; that of the alcoholic solution, $[\alpha]_D = +1{\cdot}7°$. The *isobutylic* salt has a sp. gr. = 1·028 at 18°. The sp. rotatory power at 16° is $[\alpha]_D = +5{\cdot}7°$; that of the alcoholic solution, $[\alpha]_D = +6{\cdot}0°$.

The specific rotatory powers thus vary much in the same sense as those of the corresponding normal compounds; alcohol, however, has a depressing effect in the first terms of the isobutylic series. Propyl has greater weight than isopropyl, whilst the opposite is the case with the butyls and butyryls, as already observed by Frankland and Macgregor in the case of the glycerates.

The author calculates the moments of the substituted chains by a modification of Guye's method, assuming that the bond between two singly-linked carbon tetrahedra is perfectly mobile; the figures obtained for propyl and isopropyl are in the ratio of 159 to 146, thus according in sense with the specific rotatory powers, but those calculated for butyl (or butyryl) and isobutyl (or isobutyryl) are in the ratio of 473 to 460, and are directly opposed in sense to the experimental results. JN. W.

Action of Sodium on Ethylic Aconitate and Citrate. By PAUL C. FREER (*Amer. Chem. J.*, 1895, **17**, 31—33).—Sodium and sodium ethoxide both act on each of these salts, with evolution of hydrogen.

With the aconitate, two sodium derivatives appear to be formed, of which one has probably the formula $C_{22}H_{28}O_{11}Na_4$. With dilute sulphuric acid, both sodium compounds yield a ketone of the formula $C_9H_{12}O_5$, which forms a non-crystallisable compound with phenylhydrazine. The derivative from ethylic citrate appears to be similar in character. These reactions are similar to those obtained by Dieckmann (Abstr., 1894, i, 172 and 324) from tiglic and pimelic acids, and are being further studied. L. T. T.

Allofurfurylacrylic acid. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 129—134; compare Abstr., 1894, i, 173).—The substance hitherto described as allofurfurylacrylic acid, melting indefinitely at 83—87°, still contains a small amount of furfurylacrylic acid melting at 141°. This can be removed by converting the allo-acid into its piperidine salt, and recrystallising this from benzene, in which the salt of the allo-acid is much less soluble than that of furfurylacrylic acid itself. The recrystallised salt, on decomposition, yields an allo-acid which is free from furfurylacrylic acid and melts at 103—104° quite sharply. The mother liquors from the allo-salt were found to contain small, but quite recognisable amounts of furfurylacrylic acid. The pure acid is not so readily converted into the isomeric form by heating with benzene as the impure form which has hitherto been described. The separation of the small amount of furfurylacrylic acid from the allo-acid melting at 83—87° cannot be effected by direct recrystallisation.

The heat of combustion of the impure allo-acid (m. p. 82—86°) is 761·6 Cal., and its electrolytical conductivity (100 *K*) 0·00782, the corresponding constants for furfurylacrylic acid being 757·3 Cal. and 0·00325. A. H.

Derivatives of Unsymmetrical Tribromobenzene. By C. LORING JACKSON and F. B. GALLIVAN (*Ber.*, 1895, **28**, 190—191).—Tribromodinitrobenzene (m. p. 135°), when reduced with zinc and hydrochloric acid, yields a bromophenylenediamine (m. p. 95°), which gives a tetrabromo-derivative melting at 214°; both these substances have been previously prepared from dinitrotetrabromobenzene [$(NO_2)_2 = 1:3$], and therefore the original tribromodinitrobenzene has the constitution usually assigned to it, namely [$(NO_2)_2 : Br_3 = 1:3:2:4:5$]. With sodium ethoxide the compound yields a tribromodiethoxybenzene, melting at 158°. *Bromodinitrodianilidobenzene* melts at 191—192°. Tribromonitrobenzene [$NO_2 : Br_3 = 1:3:4:5$], on reduction, yields *tribromaniline*, which melts at 80°, and yields tetrabromobenzene (m. p. 174—175°), showing that the commonly accepted constitution for the latter compound is correct.

J. B. T.

Reduction of Orthonitrobenzonitrile. By JOHANNES PINNOW and ERICH MÜLLER (*Ber.*, 1895, **28**, 149—160).—1 : 2-Nitrobenzonitrile, $NO_2 \cdot C_6H_4 \cdot CN$, was prepared from orthonitraniline by Sandmeyer's reaction; with hydroxylamine hydrochloride and alcoholic sodium methoxide, it yields a colourless *amidoxime*, $NO_2 \cdot C_6H_4 \cdot C(NH_2) : NOH$, melting at 146° (uncorr.). When reduced with tin and hydrochloric acid at the ordinary temperature, it yields 1 : 2-*amidobenzonitrile*, $NH_2 \cdot C_6H_4 \cdot CN$,

together with some amidobenzamide; the amidonitrile melts at 46—47°, and boils at 264—266° under 760 mm. pressure; it is itself unstable in air, but its *hydrochloride* is stable. The substance described by Hübner and Baerthlein (Abstr., 1878, 140) as ortho-amidobenzonitrile, was in reality a mixture of that substance with orthoamidobenzamide.

When 1 : 2-nitrobenzonitrile is heated with methyl-alcoholic soda, it is converted into 1 : 2-methoxybenzamide, $OMe\cdot C_6H_4\cdot CONH_2$; this melts at 128—129°, and was found to be identical with the amide prepared from 1 : 2-methoxybenzoic acid. The *chloride* of this acid, $OMe\cdot C_6H_4\cdot COCl$, is a liquid boiling at 254° under 760 mm. pressure.

When 1 : 2-nitrobenzonitrile is boiled with very dilute (2 per cent.) hydrochloric acid, and tin gradually added, it is reduced to 1 : 2-*azoxybenzonitrile*, $O<\begin{matrix}N\cdot C_6H_4\cdot CN\\ |\\ N\cdot C_6H_4\cdot CN\end{matrix}$; this crystallises in red needles, and melts at 194—195°; it is hydrolysed by strong hydrochloric acid at 180—190° to 1 : 2-*azoxybenzimide*, $O<\begin{matrix}N\cdot C_6H_4\cdot CO\\ |\\ N\cdot C_6H_4\cdot CO\end{matrix}>NH$, which crystallises in brown prisms, and does not melt below 320°.

When 1 : 2-nitrobenzonitrile is reduced at 30° with dilute acetic acid and zinc dust, 1 : 2-amidobenzamide, $NH_2\cdot C_6H_4\cdot CONH_2$, is formed (its *stannochloride* melts at 174°), and also some 1 : 2-azoxybenzonitrile, together with a basic substance that appears to have the formula $C_6H_4<\begin{matrix}C(NH_2)\cdot N:C\\ |\qquad\qquad |\\ N\text{———}N\end{matrix}>C_6H_4$, and, if so, is *diphenyleneamidopyrodiazoline*. This substance and its *hydrochloride* crystallise in yellow needles, and melt respectively at 221° and 277°; it yields yellow *monacetyl* and *monobenzoyl derivatives*, melting at 269—270° and 255—256° respectively. When it is hydrolysed with strong hydrochloric acid at 180°, a substance, $C_{14}H_9N_3O$, is formed; this crystallises in yellow prisms, begins to sublime at 320°, and has the properties of a phenol (its yellow *methylic ether* melts at 214°); the hydrolysis has doubtless effected the displacement of NH_2 by OH. If the phenolic substance is nitrated, or even if it is treated with nitrous acid, a NO_2 group is introduced, and a substance, $C_{14}H_8N_4O_3$, is obtained, which crystallises in yellow needles, and does not melt below 320°. The same product is obtained if the original base, or its acetyl derivative, is treated in boiling acetic acid solution with sodium nitrite; the introduction of a NO_2 group, and displacement of NH_2 by OH, must thus take place simultaneously in this reaction.

The melting and boiling points given above are uncorrected.

C. F. B.

Action of Nitrosodimethylaniline on Tertiary and Secondary Aromatic Amines in presence of Concentrated Hydrochloric acid (and Formaldehyde). By Richard Möhlau and Arthur Neubert (*Ber.*, 1895, **28**, 324—327).—The compounds previously termed hexamethyltriamidophenylacridine and octomethyltetramidophenylacridine (Abstr., 1893, i, 470) prove to be *biparadimethylamidobenzylideneparaphenylenediamine*,

$$\overset{4}{\mathrm{N}}\mathrm{Me_2}\cdot\mathrm{C_6H_4}\cdot\overset{1'}{\mathrm{C}}\mathrm{H}:\mathrm{N}\cdot\mathrm{C_6H_4}\cdot\overset{1}{\mathrm{N}}:\mathrm{CH}\cdot\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2},$$

and *paradimethylamidobenzylideneparamidodimethylaniline*,

$$\overset{4}{\mathrm{N}}\mathrm{Me_2}\cdot\mathrm{C_6H_4}\cdot\overset{1}{\mathrm{C}}\mathrm{H}:\overset{1}{\mathrm{N}}\cdot\mathrm{C_6H_4}\cdot\overset{4}{\mathrm{N}}\mathrm{Me_2}$$

(compare F. Bender, this vol., i, 109). For purposes of comparison the compound

$$\overset{3}{\mathrm{N}}\mathrm{Me_2}\cdot\mathrm{C_6H_3}<\overset{1}{\underset{6}{\mathrm{N}}}\!\!-\!\!-\!\!-

Aromatic Diazo-compounds. By HANS v. PECHMANN and LUDWIG FROBENIUS (*Ber.*, 1895, **28**, 170—176; compare Abstr., 1894, i, 283).—*Diazobenzeneparadiazotoluenetoluidide*, $C_7H_7{\cdot}N{<}^{N:NPh}_{N:N{\cdot}C_7H_7}$, seems to be formed when, in methyl alcoholic solution in the presence of sodium methoxide, diazobenzene acts on paradiazoamidotoluene, or paradiazotoluene on paradiazoamidobenzenetoluene, the latter being prepared either from diazobenzene and toluidine or from diazotoluene and aniline. It is a yellow, crystalline substance, and explodes at 76°. *Diazobenzeneparadiazotolueneanilide*, $NPh{<}^{N:NPh}_{N:N{\cdot}C_7H_7}$, is obtained from paradiazotoluene and diazoamidobenzene; it crystallises in yellow needles, and explodes at 72—73°.

Bisdiazobenzeneamide and similar compounds (Abstr., 1894, i, 329) might conceivably have unsymmetrical formulæ, $NR{:}N{\cdot}N{:}N{\cdot}NHR$, instead of $NH(N{:}NR)_2$. But bisparadiazotolueneamide, when treated with sodium methoxide and methylic iodide, yields a methyl derivative which is identical with the bisdiazotoluenemethylamide, $NMe(N{:}NC_7H_7)_2$, of Goldschmidt and Badl (Abstr., 1889, 774); this speaks for the symmetrical structure of the original substance.

When paranitrodiazobenzene chloride is added to cooled concentrated ammonia, *paradinitrodiazoamidobenzene*,

$$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

is formed; it crystallises in yellow needles and melts at 228—230°. Probably the ammonium salt of the isodiazo-compound is first formed, and this yields the nitraniline, which then condenses with the diazochloride to form the diazoamido-compound.

Paranitrodiazobenzene methyl ether condenses much more readily with phenols than the sodium derivative of paranitroisodiazobenzene. It is not, therefore, like the latter substance, an isodiazo-compound, although Hantzsch thinks that it is. And in general the authors, in opposition to Hantzsch, regard the diazo- and isodiazo-compounds as structurally, and not merely geometrically, isomeric. C. F. B.

Alkylic Diazosalts. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 225—244).—These were prepared by allowing the alkylic iodide in ethereal solution to remain, at 0° and in the dark, in contact with the normal silver diazo-salt, $C_6H_5{\cdot}N{:}N{\cdot}OAg$, or iso-diazo-salt, $C_6H_5{\cdot}NAg{\cdot}NO$. Much iodo-compound (for example, iodobenzene) is also formed, especially when the normal diazo-salt is used; indeed the alkylic salts can often only be prepared from the isodiazo-compounds, and yet their reactions show that they are all normal, and not iso-, diazo-compounds. Potash hydrolyses them to normal potassium diazo-salt (except when the latter is known to readily undergo a molecular transformation); boiling dilute sulphuric acid converts them into phenol, alcohol and nitrogen; and they condense, even at temperatures below the atmospheric, with aromatic amines to form diazoamido-compounds, and with α-naphthylamine, α-naphthol, and other aromatic bases and phenols, to form azo-colouring matters. There is not the least reason to suppose that a substance with the properties of

Hantzsch's "anti" alkylic diazo-salts is ever formed; and the isodiazo-compounds are certainly nitrosamines, and structurally, not merely geometrically, isomeric with the normal diazo-compounds. The alkylic diazo-salts form in most cases colourless or yellowish oils; they are very unstable, and even explode if kept in tightly closed vessels. The following were prepared:—

Diazobenzene methyl ether, $C_6H_5{\cdot}N{:}N{\cdot}OMe$. *Parabromodiazobenzene methyl ether*, $C_6H_4Br{\cdot}N{:}N{\cdot}OMe$. *Diazonaphthalene methyl ether*, $C_{10}H_7{\cdot}N{:}N{\cdot}OMe$. *Orthonitrodiazobenzene methyl ether*,

$$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OMe[1:2];$$

like the para-compound, undergoes molecular transformation when hydrolysed with potash, yielding the potassium iso-salt. *Orthonitrodiazoamidobenzene*, $NO_2{\cdot}C_6H_4{\cdot}N{:}NHPh$ [1 : 2], crystallises in orange-yellow needles and melts at 104·5—105°. *Paranitrodiazobenzene ethyl ether*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OEt$ [1 : 4], crystallises in white, nacreous plates melting at 24°; the *methyl ether* (compare Pechmann and Frobenius, Abstr., 1894, i, 283). *Orthomethylparanitrodiazobenzene methyl ether*, $NO_2{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}OMe$ [N : Me : NO_2=1 : 2 : 4], forms yellowish needles melting at 94°; the *ethyl ether* is an oil. *Orthomethylparanitrodiazoamidobenzene*, $NO_2{\cdot}C_6H_3Me{\cdot}N{:}NHPh$, crystallises in yellow needles, and melts at 122°. The author thinks that in normal diazo-salts (chlorides, &c.) the nitrogen atom joined to the negative group must be quinquevalent, as is indicated by the formula $R{\cdot}N{:}N{\cdot}X$, where the + and − ions are respectively ($R{\cdot}N{:}N$) and X. Or the Blomstrand-Strecker-Erlenmeyer formula, $N{:}NR{\cdot}X$, might be given. To the "labile" (Hantzsch's "syn") potassium diazobenzenesulphonate might be assigned the formula $NPh{:}N{\cdot}SO_3K$ [ions ($NPh{:}N{\cdot}SO_3$) and K], or the V. Meyer-Jacobson formula, $N{:}NPh{\cdot}SO_3K$. C. F. B.

d-**Glucosebenzoylhydrazone.** By HEINRICH WOLFF (*Ber.*, 1895, **28**, 160—163).—Aldoses react with acid hydrazides in accordance with the equation $R{\cdot}CO{\cdot}NH{\cdot}NH_2 + O{:}CH{\cdot}R' = R{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}R' + H_2O$, when the two substances are heated together in alcoholic solution; the compounds formed crystallise in white needles, and are decomposed by boiling with water.

d-*Glucosephenylsulphonehydrazone*, $Ph{\cdot}SO_2{\cdot}NH{\cdot}N{:}C_6H_{12}O_5$, melts with decomposition at 154—155°; boiling with water converts it into dextrose, biphenylsulphonehydrazone, $N_2H_2(SO_2Ph)_2$, (and hydrazine?), a violent evolution of gas taking place.

d-*Glucosebenzoylhydrazone*, $CPhO{\cdot}NH{\cdot}N{:}C_6H_{12}O_5$, melts and decomposes at 171—172°; boiling with water converts it into *d*-glucose and benzoylhydrazine. The latter can be precipitated as benzylidenebenzoylhydrazine by the addition of benzaldehyde, and the *d*-glucose can then be recovered from the solution. These reactions afford a means of isolating *d*-glucose from invert-sugar, for *l*-fructose, being a ketose and not an aldose, does not react with benzoylhydrazine.

C. F. B.

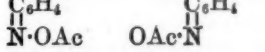
Reduction of Aromatic Nitro-compounds. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 245—251; compare Abstr., 1894, i, 373).—A preliminary notice, published prematurely owing to invasion of the author's territory by Lumière and Seyewetz (*Bull. Soc. Chim.*, 1894, [3], **11**, 1038). *Paratolylhydroxylamine*, $C_6H_4Me{\cdot}NH{\cdot}OH$ [1 : 4], forms nacreous plates, melting at 93·5—94°; it oxidises in air to para-azoxytoluene, and is converted by nitrous acid into a *nitrosamine*, which crystallises in white needles melting at 59—59·5°, and further into paradiazotoluene nitrate; hot dilute sulphuric acid converts it into paratoluquinol [$Me : (OH)_2 = 3 : 1 : 4$]; and oxidising agents into *paranitrosotoluene*, $C_6H_4Me{\cdot}NO$, which crystallises in white needles, melts at 48·5° to a green liquid, and yields green solutions.

Metatolylhydroxylamine crystallises in white, silky plates, and melts at 68°. The *nitrosamine* crystallises in white needles, which melt at 54—54·5°; *metanitrosotoluene* forms white needles which melt at 53—53·5° to a green liquid, and yield green solutions.

Orthotolylhydroxylamine is an oil, and yields a *nitrosamine*. *Orthonitrosotoluene* crystallises in white needles, melts at 72—72·5° to a green liquid, and yields green solutions.

Nitro-derivatives of halogenbenzenes, of benzylic chloride, of benzaldehyde, and of benzoic acid appear to yield hydroxylamines when boiled with zinc dust and water. Nitranilines are reduced to diamines, and nitrophenols to amidophenols. C. F. B.

Stereoisomeric Derivatives of Quinonedioximes. By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 340—343).—Diacetylquinonedioxime exists in two isomeric forms. The more stable of these is formed when quinonedioxime is boiled with sodium acetate and acetic anhydride for some minutes. It crystallises in compact, leaf-like plates, is only sparingly soluble in benzene, and melts at 190°. The less stable form is obtained when the mixture of quinonedioxime, sodium acetate, and acetic anhydride is heated just to boiling, and then immediately cooled. It is readily soluble in benzene, from which it crystallises in long, lustrous needles containing benzene, but the latter is rapidly lost on exposure to the air. It melts at 147°, when rapidly heated, but the melting point quickly rises, owing to partial conversion into the isomeride. When boiled with benzene for some time, it is also converted into the isomeride. Both the forms have the normal molecular weight as determined by the cryoscopic method, and both yield the same quinonedioxime when hydrolysed. It is probable that the substance of lower melting point is the syn-derivative, the higher being the anti-form.



Thymoquinone also appears to yield two isomeric acetates. Quinonedioxime itself is known to crystallise in two different forms, but it is at least doubtful whether these are stereoisomeric modifications.

A. H.

Imidazolones and their Decomposition Products. By HANS RUPE (*Ber.*, 1895, **28**, 251—260; compare Abstr., 1894, i, 241).—Formylbenzoylcarbamide, NHBz·CO·NH·CHO, is formed by the action of nitric acid of sp. gr. 1·405 on phenylimidazolone in acetic acid solution. It crystallises in long, flat needles melting at 161°. When boiled with dilute alcoholic hydrogen chloride, or treated with cold aqueous soda, it is converted into formic acid and benzoylcarbamide, which melts, when pure, at 215°, and not at 208°, as hitherto supposed (*Zeit. f. Chem.*, 1868, 305).

If only 1 mol. of nitric acid be employed, nitrophenylimidazolone is formed. This crystallises in lustrous, yellow plates, which decompose at 203—207°, according to the rapidity with which they are heated. This substance has acid properties, and is not altered by boiling with water or dilute alkalis, although with acids a deep-seated decomposition takes place after some time.

Bromine reacts with phenylimidazolone to produce the *ureïde of parabromobenzoylformic acid*, $C_6H_4Br·CO·CO·NH·CO·NH_2$, which forms small, lustrous prisms melting at 186·5°. It is very stable towards acids, and dissolves without alteration in dilute alkalis, but is decomposed when boiled with them, carbamide being produced, along with benzoylformic acid. The *hydrazone* of the ureïde crystallises in slender, yellow needles, and melts at 151°. On reduction with sodium amalgam at 40°, the ureïde is quantitatively converted into carbamide and mandelic acid. *Parabromobenzoylformic acid* forms small plates, which have a satiny lustre, and melt at 108°. The *sodium* salt is only sparingly soluble in water, and is precipitated from a concentrated solution of the acid by aqueous soda. The acid, like benzoylformic acid itself, gives a reddish-violet coloration with sulphuric acid and benzene containing thiophen. The *hydrazone* of the acid forms yellow needles melting at 180·5°. The acid is reduced by sodium amalgam to mandelic acid, and is oxidised by silver oxide to parabromobenzoic acid, its constitution, and that of the ureïde, being thus proved.

Methylic parabromobenzoate crystallises in long, white needles, has an extremely pleasant, fruity odour, and melts at 81°. A. H.

Oil of Mignonette Root. By JULIUS BERTRAM and HEINRICH WALBAUM (*J. pr. Chem.*, 1894, [2], **50**, 555—561).—The root of *Reseda odorata*, L., yields an oil, on distillation, which smells of radishes, has a light brown colour, a sp. gr. of 1·067 at 15°, and a rotation of +1° 30′ in a 100-mm. tube. This oil is phenylethylthiocarbimide, for, when heated with strong hydrochloric acid, it yields phenylethylamine hydrochloride, carbon oxysulphide and hydrogen sulphide being evolved; phenylethylthiocarbamide is produced when it is heated with alcoholic ammonia. The authors find that diphenylethyloxamide melts at 186°, and phenylethylthiocarbamide at 137°, whilst Neubert (Abstr., 1886, 873) gives 180° and 123° respectively for these constants. They have synthesised phenylethylthiocarbimide, and find that its reactions are in accord with those of mignonette-root oil. A. G. B.

Isophenolphthaleïn and Allofluoresceïn. By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 108—109).—In this preliminary notice, the author describes compounds obtained by the action of phthalic chloride on phenols, and isomeric with the phenolphthaleïns.

Isophenolphthaleïn crystallises in slender, white needles melting at 69—70°, and is not coloured by alkalis. Its constitution is probably represented by the formula $CO<^{O\ \ -}_{C_6H_4}>C(OPh)_2$. Catechol and quinol react with 1 mol. of the chloride to form substances of a similar constitution. Resorcinol, on the other hand, yields two compounds, $CO<^{O\ \ -}_{C_6H_4}>C<^{O}_{O}>C_6H_4$ and $CO<^{O\ \ -}_{C_6H_4}>C(O\cdot C_6H_4\cdot OH)_2$. These both give green, fluorescent solutions with potash, but differ markedly from fluoresceïn itself. A. H.

Constitution of the Safranines. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 270—276).—The action of nitrosodimethylaniline hydrochloride on metahydroxydiphenylamine yields a black colouring matter which probably belongs to the oxazine group. In the presence of a mineral acid, on the other hand, a carmine-red colouring matter, *dimethylsafraninone*, $O:C_6H_3<^{N\ \ -}_{NPh}>C_6H_3\cdot NMe_2,HCl$, is formed; this is a brownish-red, crystalline powder, which yields a red solution with water, and dissolves in alcohol forming an orange-red solution with a yellow fluorescence. Aqueous soda precipitates the base, which is of no industrial importance. The formation of the substance takes place in two stages, a blue indophenol being formed as an intermediate product.

Safraninone, $O:C_6H_3<^{N\ \ -}_{NPh}>C_6H_3\cdot NH_2,HCl$, may be obtained in a similar manner, but is best prepared by the oxidation of a mixture of paraphenylenediamine and metahydroxydiphenylamine in molecular proportion; it is also formed in very small quantity when safranol is heated with ammonia at 180°. The crystals have a green lustre, but in other respects resemble those of the dimethyl-derivative. It contains an amido-group, and forms a blue diazo-compound, which reacts with β-naphthol to form a blue colouring matter. When the amido-group is eliminated, *safranone*, $O:C_6H_3<^{N\ \ -}_{NPh}>C_6H_4$, is produced; this is also formed when "safranid" (azosafranine) is heated with 75 per cent. sulphuric acid. It crystallises in small, brown needles, and yields a magenta-coloured solution with hot water. All the three compounds just described exhibit dichroïsm when dissolved in concentrated sulphuric acid.

Safranol, $O:C_6H_3<^{N\ \ -}_{NPh}>C_6H_3\cdot OH$, is formed when metahydroxydiphenylamine is heated with paranitrosophenol and aqueous soda, and may also be obtained by oxidising a mixture of paramidophenol and metahydroxydiphenylamine in presence of mineral acids. The formation of safranol by these methods supplies the proof that safranine contains the amido-group in the meta-position.

A safranine synthesis can be carried out, in complete agreement with this conclusion, by heating metamidoditolylamine, obtained from paraditolylamine, with quinone dichlorimide in acetic acid solution. The new safranine has the formula

$$HCl,HN{:}C_6H_3\!<\!\overset{N}{\underset{N(C_6H_4Me)}{\diagdown\!\!\diagup}}\!>\!C_6H_2Me{\cdot}NH_2,$$

and is isomeric with the safranine T of commerce. It is obtained as the hydrochloride, and forms a beetle-green powder, which yields fluorescent solutions. The colour produced on cotton mordanted with tannin cannot be distinguished from that obtained with safranine T. A. H.

The Fluorindines. By Otto Fischer and Eduard Hepp (*Ber.*, 1895, **28**, 293—301; compare Abstr., 1890, 1444).—The red oxidation product of orthamidophenol, described by Fischer and Jonas (this vol., i, 25) as having the formula $C_{12}H_8N_2O_2$, is identical with the compound obtained by Zincke and Hebebrand (Abstr., 1885, 258) by the oxidation of the same substance with quinone, to which, however, they assigned the formula $C_{24}H_{18}N_4O_4$. The determination of the molecular weight by the cryoscopic method, using phenol as a solvent, shows that the molecular formula is $C_{12}H_8N_2O_2$, so that the substance is probably amidobenzeneazoxindone. It contains a primary amido-group, and reacts with aldehydes like a primary base. The compound thus formed with salicylaldehyde crystallises in needles, which have a golden lustre, and melt above 300°. When the red compound is fused with orthamidophenol hydrochloride, it yields triphendioxazine, as previously described.

Triphenazinoxazine, $C_6H_4\!<\!\overset{NH}{\underset{N}{\diagdown\!\!\diagup}}\!>\!C_6H_2\!<\!\overset{N}{\underset{O}{\diagdown\!\!\diagup}}\!>\!C_6H_4$, is readily formed when asymmetric dioxyphenazine is treated in the same manner, and when the red compound, described above, is fused with orthophenylenediamine. It forms indistinctly crystalline aggregates, and yields fluorescent solutions.

Diphenylhomofluorindine (fluorindine) may be synthetically obtained by fusing the oxidation product of orthamidodiphenylamine (diphenyldiamidophenazine) with orthophenylenediamine hydrochloride. A good yield of the fluorindine is thus obtained.

Fluorindine can also be obtained synthetically by the oxidation of phenylinduline, dissolved in nitrobenzene, with mercuric oxide. A 10 per cent. yield is obtained, and the nitrobenzene seems to influence the reaction, as when other solvents are used a different fluorindine is obtained.

Fluorindine is, however, best prepared by oxidising, with mercuric oxide, azophenine dissolved in nitrobenzene.

The authors also maintain the formulæ which they have ascribed to triphenodioxazine, homofluorindine, and the fluorindines, against the criticism of Nietzki (*Chemie der organ. Farbstoffe*, II, Aufl., p. 230). A. H.

Iodonium Bases from Parachloriodobenzene. By L. W. WILKINSON (*Ber.*, 1895, **28**, 99—101).—*Iododichlorodiphenyliodonium hydroxide*, $C_6H_3ICl{\cdot}I(OH){\cdot}C_6H_4Cl$, prepared in a similar manner to the diphenyl compound (Abstr., 1894, i, 461), is only known in aqueous solution. The *iodide* is colourless and crystalline, becomes yellow on exposure to air, and melts and decomposes at 133°. The *chloride* forms colourless plates, and the *bromide* granular crystals, melting at 195° and 190° respectively. The *nitrate* crystallises in colourless needles, melting and decomposing at 188°. The *periodide* forms brown, lustrous needles melting at 152°. The *sulphide* is yellow and unstable; the *platinochloride* is deposited in reddish-yellow crystals, and melts at 160°.

Dichlorodiphenyliodonium hydroxide, $OH{\cdot}I(C_6H_4Cl)_2$, obtained together with the preceding base, only exists in aqueous solution. The *iodide* forms colourless, flocculent crystals melting at 163°. The *chloride* crystallises in colourless plates, the *bromide* and *nitrate* in needles, they melt at 202°, 190°, and 200° respectively. The *dichromate* is orange-yellow, unstable, and melts and decomposes at 149°. The *mercurochloride* is deposited in colourless, flocculent crystals, the *platinochloride* in reddish needles; they melt at 169° and 184° respectively. J. B. T.

Iodonium Bases from Pariodotoluene. By JOHN MCCRAE (*Ber.*, 1895, **28**, 97—99).—The following compounds were prepared in a similar manner to the phenyl derivatives described by Hartmann and v. Meyer (Abstr., 1894, i, 461). *Ditolyliodonium hydroxide*, $OH{\cdot}I(C_6H_4Me)_2$, is only known in aqueous solution, and is formed in small quantity in the preparation of iodo- and iodoso-toluene. The *iodide* is colourless, becomes yellow on exposure to light, and melts at 146°. The *chloride* and *bromide* crystallise in needles and both melt at 178°. The *dichromate* is deposited in reddish-yellow plates, and explodes when heated. The *periodide* crystallises in highly lustrous, dark red needles, and melts at 156°. The *nitrate*, *mercurochloride*, and *bromo-mercurochloride* crystallise in needles, and melt at 139°, 179°, and 189° respectively. The *aurochloride* and *platinochloride* are deposited in plates; the former melts at 126°, the latter at 176°, with decomposition. By the action of sodium or ammonium sulphide on ditolyliodonium hydroxide, iodotoluene, and paraditolylic sulphide are formed in the proportion of two molecules to one.

The base, $C_6H_3IMe{\cdot}I(OH){\cdot}C_6H_4Me$, is only known in aqueous solution. The *iodide* melts and decomposes at no definite temperature. The *chloride* and *bromide* are amorphous, and melt at 165·5° and 163° respectively. The *dichromate* is unstable, and melts at 154°; the *mercurochloride* crystallises in small plates, and melts and decomposes at 149°. J. B. T.

Derivatives of Paradimethylamidobenzaldehyde. By FRITZ BENDER (*Ber.*, 1895, **28**, 109—111).—Möhlau has described two colouring matters obtained by the action of dimethylaniline on nitrosodimethylaniline in hydrochloric acid solution in the presence of formaldehyde. The first of these, rubifuscine, to which he ascribed the

constitution of hexamethyltriamidophenylacridine, is decomposed, when the hydrochloride is boiled with water, into paradimethylamidobenzaldehyde and phenylenediamine. The second compound, named by Möhlau octomethyltetramidophenylacridine, is decomposed under similar conditions into dimethylamidobenzaldehyde and paramidodimethylaniline. The two colouring matters are, moreover, formed when the aqueous solutions of the hydrochlorides of their decomposition products are mixed. A. H.

Paraïsobutylsalicylaldehyde and its Derivatives. By F. B. Dains and I. R. Rothrock (*Amer. Chem. J.*, 1894, **16**, 634—645; compare Bradley, Abstr., 1892, 1458).—*Paraïsobutylsalicylaldehyde*, $C_4H_9{\cdot}C_6H_3(OH){\cdot}COH$ [OH : COH : C_4H_9 = 1 : 2 : 4], is obtained on heating a mixture of isobutylphenol (45 grams), sodium hydroxide (45 grams), chloroform (55 grams), and water (500 c.c.) in a water bath for two hours. The aldehyde is readily separated from the unchanged isobutylphenol by treating the product with phenylhydrazine, which gives with the former a well-characterised solid hydrazone. This is readily reconverted into the aldehyde on treatment with sulphuric acid and subsequent steam distillation. The pure aldehyde is a yellow, highly refractive oil, with an aromatic odour resembling that of salicylaldehyde. It boils, decomposing slightly, at 251—252° under a pressure of 729 mm., and does not solidify at −18°; sp. gr. = 1·039 at 20°. It dissolves in all the common organic solvents, and forms a violet-coloured solution with ferric chloride. From a neutral solution of the sodium derivative, copper sulphate throws down a yellowish-green precipitate, and silver nitrate, lead acetate, calcium chloride, and barium chloride throw down white precipitates. The *phenylhydrazone*, $C_4H_9{\cdot}C_6H_3(OH)CH{:}N{\cdot}NHPh$, crystallises from light petroleum in thin, golden, monoclinic plates, melts at 178°, and yields a *diacetyl derivative*, $C_4H_9{\cdot}C_6H_3(OAc)CH{:}N{\cdot}NAcPh$, which crystallises in small, white needles, and melts at 128°. The *aniline derivative*,

$$C_4H_9{\cdot}C_6H_3(OH)CH{:}NPh,$$

crystallises from alcohol in yellow, monoclinic plates, and melts at 87°. The *aldoxime*, $C_4H_9{\cdot}C_6H_3(OH)CH{:}NOH$, crystallises from light petroleum in long, monoclinic needles, melts at 112°, yields a *dibenzoyl* derivative which melts at 160°; and, on treatment with acetic anhydride, forms the *acetyl* derivative of *paraïsobutylsalicylonitrile*, $C_4H_9{\cdot}C_6H_3(OAc){\cdot}CN$, a pale yellow oil, which on hydrolysis with potash forms *paraïsobutylsalicylonitrile*, $C_4H_9{\cdot}C_6H_3(OH){\cdot}CN$; this crystallises in slender, white, monoclinic needles.

The *methyl* derivative of *paraïsobutylsalicylaldehyde* boils at 274—276°, at a pressure of 735 mm., the *benzyl* derivative crystallises in long, slender, monoclinic prisms, which melt at 70—71°. *Ethylic paraïsobutylsalicylaldehydecarboxylate*, $COH{\cdot}C_6H_3(C_4H_9){\cdot}COOEt$, melts at 63°. *Paradiïsobutyldisalicylaldehyde* crystallises in monoclinic needles, and melts at 158°.

Paraïsobutylorthobromosalicylaldehyde [OH : COH : C_4H_9 : Br = 1 : 2 : 4 : 6], obtained by the action of bromine on the dried sodium

derivative of paraïsobutylsalicylaldehyde, suspended in carbon bisulphide, crystallises in pale yellow, monoclinic plates, and melts at 86—87°; the corresponding *aldoxime* crystallises in white, tabular, monoclinic plates, melts at 163°, and forms a *dibenzyl* derivative, which crystallises from hot alcohol in needles and melts at 189°; the corresponding *phenylhydrazone* forms long, monoclinic crystals, and melts at 152°. G. T. M.

Constitution of the Bromocinnamic acids. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 134—137).—Glaser's α-bromocinnamic acid is converted, although with some difficulty, into ordinary cinnamic acid when it is boiled in alcoholic solution with zinc filings. This acid therefore has the stereochemical formula $\begin{matrix} Ph\cdot C\cdot H \\ \| \\ Br\cdot C\cdot COOH \end{matrix}$, which agrees well with its reactions and transformations. A. H.

Intramolecular Change in βγ-Phenylcrotonic acid. By RUDOLPH FITTIG and ALFONS LUIB (*Annalen*, 1894, **283**, 297—308).—Amongst the unsaturated βγ-acids which have been investigated, phenylcrotonic acid is distinguished by its stability towards aqueous soda, scarcely more than 10 per cent. being attacked by this reagent after many hours. *αβ-Phenylcrotonic acid*, $CH_2Ph\cdot CH{:}CH{:}COOH$, is one of the products, the yield of this substance amounting to about 1 per cent. It crystallises from benzene in nacreous plates, and melts at 65°. The *calcium* salt contains $3H_2O$, and the *barium* salt $1H_2O$. *Phenyl-β-bromobutyric acid* crystallises in short, transparent prisms, and melts at 54°. It dissolves in boiling water, giving rise to phenylpropylene and *phenyl-β-hydroxybutyric acid*, which is also formed by the action of boiling aqueous soda on βγ-phenylcrotonic acid; this crystallises from ether in colourless plates and melts at 98°. When distilled, it gives rise to a mixture of αβ- and βγ-isocrotonic acids. The *calcium* salt is anhydrous, and the *barium* salt contains $1H_2O$; the *silver* salt crystallises from hot water in thin plates. A mixture of αβ- and βγ-phenylcrotonic acids, in which the latter preponderates, is formed when phenyl-β-hydroxybutyric acid is treated with hot aqueous soda for 12 hours; 90 per cent. of unchanged acid is recoverable. M. O. F.

Intramolecular Change in Phenyl-βγ-pentenic (Hydrocinnamenylacrylic) acid. By RUDOLPH FITTIG and THEODOR HOFFMANN (*Annalen*, 1894, **283**, 308—318; compare R. Fittig and J. Stern, Abstr., 1892, 988).—*Phenyl-αβ-pentenic acid*, $CH_2Ph\cdot CH_2\cdot CH{:}CH\cdot COOH$, is readily formed when hot aqueous soda acts on the βγ-acid. It melts at 104° and forms rhombic crystals; $a:b:c = 0{\cdot}5863:1:0{\cdot}2675$. The *calcium* salt crystallises in prismatic needles which retain $3H_2O$; the *barium* salt contains $4H_2O$. The *silver* salt crystallises from hot water. The *calcium* salt of the βγ-acid contains $1H_2O$, and the *barium* salt is anhydrous.

Phenyl-αβ-dibromovaleric acid crystallises in slender needles, which melt at 139° (following abstract); sodium amalgam reduces it to

phenylvaleric acid. *Phenyl-β-bromovaleric acid* melts at 57—58°. Boiling water converts it into *phenyl-β-hydroxyvaleric acid*, which is also formed by the action of hot aqueous soda on phenyl-βγ-pentenic acid; it separates from water and from ether in prismatic crystals, which melt at 131°. The *calcium* salt is anhydrous, and the *barium* salt retains $1H_2O$. Phenyl-β-hydroxyvaleric acid is attacked slowly by hot aqueous soda, yielding 10 per cent. of phenyl-αβ-pentenic acid, which is also formed when the hydroxy-acid is distilled. M. O. F.

Brominated Acids from Phenyl-αβ-pentenic and Phenyl-βγ-pentenic acids. By RUDOLPH FITTIG and HEINRICH PERRIN (*Annalen*, 1894, **283**, 318—337; compare the preceding abstract, and R. Fittig and J. Stern, Abstr., 1892, 988).—When the solution of phenyl-β-bromovaleric acid in warm petroleum is allowed to evaporate spontaneously, two forms of crystals are deposited; one modification melts at 55—56°, whilst the other sinters at 57°, and melts completely at about 80°.

Treatment with boiling water for several hours converts phenyl-β-bromovaleric acid into a mixture of phenylbutylene, phenyl-β-hydroxyvaleric acid, phenyl-αβ-pentenic acid, and a very small quantity of phenylvalerolactone.

The action of bromine on hydrocinnamenylacrylic acid gives rise to phenyl-βγ-dibromovaleric acid, which melts at 111—112°, and crystallises in plates belonging to the asymmetric system; $a : b : c = 1{\cdot}538 : 1 : 2{\cdot}41577$. This acid is also formed when cinnamenylacrylic acid is acted on by hydrogen bromide, and when thus obtained, it melts at 113·5—114·5°; this form is less soluble than the modification of lower melting point, from which it differs also crystallographically. The crystals belong to the monosymmetric system; $a : b : c = 2{\cdot}0548 : 1 : 1{\cdot}2052$. $\beta = 69° 30'$. When boiled with aqueous sodium carbonate, it yields an unsaturated hydrocarbon and an acid which crystallises from boiling water in needles, and melts at 138°; *phenylpentenolactone*, $C_{11}H_{10}O_2$, is formed at the same time. This crystallises in plates which melt at 60°, and differs completely from phenylangelicalactone obtained from the isomeric dibromo-acid under similar conditions (*loc. cit.*). Hot aqueous alkalis convert it into salts of *phenylhydroxypentenic acid*; the *barium* and *calcium* salts are anhydrous, and the *silver* salt is decomposed by light. Phenylpentenolactone is unsaturated, and when treated with bromine yields *phenyldibromovalerolactone*, $C_{11}H_{10}Br_2O_2$, which crystallises in silvery plates and melts at 99—100°.

Phenyltetrabromovaleric acid is obtained by the action of bromine on cinnamenylacrylic acid; it forms a crystalline powder which melts at 243°, with copious evolution of gas.

Phenyldibromopentenic acid, CHPh:CH·CHBr·CHBr·COOH, is obtained by adding to the solution of cinnamenylacrylic acid in ether and carbon bisulphide the calculated amount of bromine in the latter solvent; it forms colourless, transparent crystals, which lose hydrogen bromide when recrystallised. M. O. F.

Oxidation Products of Phenyl-$\beta\gamma$-pentenic and Phenyl-$\alpha\beta$-pentenic acids. By RUDOLPH FITTIG and ERNST MAYER (*Annalen*, 1894, **283**, 337—341; compare Abstr., 1892, 986).—Phenyl-$\beta\gamma$-dihydroxyvaleric acid (*loc. cit.*) crystallises in long needles which melt at 110°, readily undergoing conversion into phenylvalerolactone.

Phenyl-$\alpha\beta$-dihydroxyvaleric acid is obtained by oxidising phenyl-$\alpha\beta$-pentenic acid with potassium permanganate; it crystallises from water in needles, and melts at 156·5° without giving rise to the lactone. The *barium* salt is anhydrous, and the *calcium* salt forms colourless, silky plates which contain $1H_2O$; the *silver* salt is a crystalline powder. M. O. F.

α- and β-Isatropic acids. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 137—143).—When α-isatropic acid, dissolved in alcohol, is treated with hydrogen chloride, without cooling, *ethylic hydrogen isatropate*, $COOH\cdot C_6H_{14}\cdot COOEt$, separates; it crystallises in small plates melting at 186°. When boiled with aqueous 33 per cent. potash, it is converted into a mixture of 1 part of α-isatropic acid and 2 parts of β-isatropic acid. When β-isatropic acid is treated with hydrogen chloride in a similar manner, a substance is obtained which, on decomposition with potash, yields β-isatropic acid. After repeated crystallisation from acetic acid, however, this becomes identical with the ethylic hydrogen isatropate obtained directly from α-isatropic acid, and behaves in the same manner towards aqueous potash. It is therefore probable that ethylic hydrogen β-isatropate is first formed and is then converted by repeated crystallisation into the corresponding α-compound.

If α-isatropic acid is heated at 70° with alcoholic hydrogen chloride, a normal *ethylic salt*, $C_6H_{14}(COOEt)_2$, is formed; this substance melts at 78—79°, whereas, according to Fittig (*Annalen*, **206**, 34), normal ethylic α-isatropate melts at 180—181°, and is formed by simply passing hydrogen chloride into an alcoholic solution of the acid. The normal ethylic salt obtained by the author yields, on hydrolysis with alcoholic potash, a mixture of acids containing about 20—30 per cent. of the α-acid and 80—70 per cent. of the β-acid. It seems probable that the relations between these two acids are to be explained by stereochemical considerations, and, indeed, an examination of the formulæ put forward as probable by Fittig shows that cis-trans-isomerism is possible. The author's researches in this direction are not yet completed. A. H.

Condensation of Toluquinone with Ethylic Acetoacetate. By CARL GRAEBE and SIEGMUND LEVY (*Annalen*, 1894, **283**, 245—268).—*Hydroxydimethylisocoumarilic acid*, $OH\cdot C_6H_2Me<\begin{matrix}C(COOH)\\O\text{———}\end{matrix}>CMe$, crystallises in needles which decompose at 280°. It is obtained from the *ethylic* salt, which is produced when a mixture of toluquinone and ethylic acetoacetate is heated with acetone and zinc chloride; it crystallises in colourless pyramids which melt at 173°, and it dissolves in concentrated sulphuric acid, with development of an intense blue coloration which gradually becomes brown. The ethylic salt gives rise

to an *acetyl* derivative which crystallises in large, colourless needles, and melts at 96°; the *benzoyl* derivative melts at 94—95°. The *bromo*-derivative melts at 208°, and yields an *acetyl* derivative which melts at 137—138°. The *dibromo*-derivative melts at 123—124°, and the *tribromo*-derivative 145°; these derivatives also have been acetylated. The *dichloro*-derivative melts at 134—135°, and yields an *acetyl* derivative which melts at 138—139°; it is converted by the action of 10 per cent. aqueous soda into *hydroxydimethyldichlorocoumarilic acid*, which decomposes at 260—270° and yields a *barium* salt containing $2H_2O$. The *trichloro*-derivative, $O{:}C_6Cl_3Me{<}^{C(COOEt)}_{O\text{———}}{>}CMe$, melts at 103°.

The dichloro- and trichloro-derivatives, when oxidised with dilute nitric acid, yield the *orthoquinone* derivative of the ethylic salt of dimethylchlorisocoumarilic acid, which has the constitution

$$C_6ClMeO_2{<}^{C(COOEt)}_{O\text{———}}{>}CMe;$$

it crystallises in deep red plates which melt at 118—119°, and dissolves in concentrated sulphuric acid with development of a violet coloration gradually changing to dark blue. On reducing this compound, dihydroxydimethylchlorisocoumarilic acid is obtained in the form of the *ethylic* salt; this melts at 170—171°, and yields a *diacetyl* and a *dibenzoyl* derivative which melt at 136° and 174—175° respectively. The *quinoxaline* derivative,

$$C_6H_3Me{<}^{N}_{N}{>}C_6ClMe{<}^{C(COOEt)}_{O\text{———}}{>}CMe,$$

is obtained by the action of orthotoluylenediamine on the ethylic salt. It crystallises in reddish-violet needles melting at 162°.

The *ethylic* salt of *trimethylbenzodifurfuranedicarboxylic acid*,

$$CMe{<}^{O\text{———}}_{C(COOH)}{>}C_6HMe{<}^{C(COOH)}_{O\text{———}}{>}CMe,$$

is formed, in addition to the ethylic salt of hydroxydimethylisocoumarilic acid, when a mixture of toluquinone and ethylic acetoacetate is heated with zinc chloride. It melts at 133°, and gives rise to a *bromo*-derivative. The *acid* itself is obtained in needles which melt at 220°; the *potassium* salt is anhydrous, and the *sodium* salt contains $4H_2O$. M. O. F.

Iodoisophthalic and Iodosoisophthalic acids. By Albert Grahl (*Ber.*, 1895, **28**, 84—90).—*Meta-iodoisophthalic acid*, [$(COOH)_2 : I = 1 : 3 : 5$], is prepared from the corresponding nitroisophthalic acid, and crystallises from acetic acid in lustrous, microscopic needles melting at 288—289°. The *silver salt* is amorphous. When potassium permanganate acts on the acid, in presence of sulphuric acid, no iodoso-derivative is formed, but the bulk of the acid is completely oxidised, and the remainder recovered unchanged. The *nitro*-deriva-

tive crystallises in slender, yellow needles. The *iododichloride*, formed by the action of chlorine on the acid in chloroform solution, is yellow, amorphous, and unstable; on treatment with soda, the original acid is regenerated.

Periodometatoluic acid, [COOH : Me : I = 1 : 3 : 4], is prepared by the oxidation of 1 : 3 : 4-iodo-xylene with nitric acid; it melts at 214—215°, and is identical with the acid mistaken for "iodoisophthalic acid" by Hammerich (Abstr., 1890, 1106). The *silver salt* is amorphous; the *iododichloride* is amorphous and unstable.

Orthiodoisophthalic acid, [$(COOH)_2$: I = 1 : 3 : 4], is obtained when the preceding acid is oxidised with potassium permanganate; it is purified by means of the dimethylic salt, and melts at 285—286°. The *silver salt* is amorphous.

Orthiodosoisophthalic acid, $C_6H_3(COOH)_2 \cdot IO$, is formed by the action of concentrated nitric acid on the iodo-acid, and crystallises in colourless, lustrous needles melting and decomposing at 269°; it readily reacts with potassium iodide at the ordinary temperature, and in general properties resembles the corresponding benzoic and terephthalic acids. The *hydrogen sodium salt* crystallises with $1H_2O$ in yellow plates; the *hydrogen silver salt* is yellow and amorphous, and explodes when heated.

The acid termed by Klingel "orthiodoisophthalic acid" (Abstr., 1886, 61) is evidently some other compound, as it melts at 203—204°.

J. B. T.

Action of Bromine on Alkylidenemalonic acids and their Ethereal Salts. By Carl T. Liebermann (*Ber.*, 1895, **28**, 143—145). —The author has confirmed the statement made by Claisen and Crismer (Abstr., 1884, 444) that benzylidenemalonic acid does not form an additive compound with bromine, whilst its ethylic salt does so slowly. This appears to be a general property of unsaturated compounds containing a doubly linked carbon atom combined with two carboxyl or similar electronegative groups. The feeble additive powers of such unsaturated acids as fumaric acid, mesaconic acid, &c., are probably to be ascribed to a similar cause, the electronegative groups being in these cases each combined with one of the doubly linked carbon atoms.

A. H.

Addition of Aniline and Phenylhydrazine to Methylic Benzylidenemalonate. By R. Blank (*Ber.*, 1895, **28**, 145—148). —It is already known that ethylic salts of the type $R \cdot CH{:}C(COOR)_2$ not only form bimolecular polymerides, but also additive compounds with 1 mol. of water, ethylic alcohol, sodium ethoxide, sodium methoxide, or ethylic malonate. It is now shown that additive compounds are also formed with aniline and phenylhydrazine.

Aniline unites with methylic hydrogen benzylidenemalonate, $CHPh{:}C(COOMe) \cdot COOH$, to form the *aniline salt* of *methylic hydrogen β-anilidobenzylmalonate*,

$$NHPh \cdot CHPh \cdot CH(COOMe) \cdot COO \cdot NH_3Ph,$$

which melts at 97·5°, and easily decomposes with formation of benz-

aldehyde. With methylic benzylidenemalonate, $CHPh{:}C(COOMe)_2$, aniline unites to form *methylic β-anilidobenzylmalonate*,

$$NHPh{\cdot}CHPh{\cdot}CH(COOMe)_2,$$

which melts at 117—118°, and yields a very unstable *hydrochloride*.

Phenylhydrazine unites with methylic benzylidenemalonate yielding *methylic β-phenylhydrazidobenzylmalonate*,

$$N_2H_2Ph{\cdot}CHPh{\cdot}CH(COOMe)_2,$$

which melts at 94·5°, and, when melted, or when boiled in absolute alcoholic solution, loses methylic malonate and forms benzylidene hydrazine, $N_2HPh{:}CHPh$. The final result is thus a displacement of methylic malonate by phenylhydrazine, as W. Wislicenus has already pointed out (Abstr., 1894, i, 465).

Ethylic benzylidenemalonate reacts with aniline and with phenylhydrazine in the same way as does the methylic salt. C. F. B.

Etherification of Aromatic Acids. By Victor Meyer (*Ber.*, 1895, **28**, 182—189).—The author has previously stated that hemimellitic acid, [$COOH_3 = 1 : 2 : 3$], should only yield a diethylic salt on treatment with alcohol and hydrogen chloride. Graebe confirms this. Chloronitrobenzoic acid, [$COOH : NO_2 : Cl = 1 : 2 : 6$], is prepared most readily from nitrotoluidine, which is first converted into chloronitrotoluene and the latter oxidised with nitric acid. The benzoic acid yields no methylic salt with hydrogen chloride and methylic alcohol; the rule applies therefore when the substituting groups are dissimilar.

Attempts to prepare an isomeric ethylic tetrachlorophthalate (compare this vol., i, 93) were unsuccessful. As previously surmised (*loc. cit.*), 2 : 1-chloronaphthalenecarboxylic acid gives no ethylic salt with alcohol and hydrogen chloride. 3 : 2-Chloronaphthalenecarboxylic acid, under similar circumstances, yields 90 per cent. of the ethylic salt; these results are contrasted with Jacobson's investigation of the formation of semidines (Abstr., 1893, i, 327). γ-Anthracenecarboxylic acid, as anticipated, gives no ethylic salt with alcohol and hydrogen chloride. Behla has previously shown that the same applies to γ-chloranthracene-γ-carboxylic acid, and Börnstein that the isomeric acid readily yields an ethylic salt. Nitrotoluidine, [$Me : NO_2 : NH_2 = 1 : 2 : 4$], was converted into the corresponding bromotoluic acid, [$Me : COOH : Br = 1 : 2 : 4$], and this was found to be identical with Racine's acid (m. p. 167°), to which he assigned the constitution [$Me : COOH : Br = 1 : 2 : 3$], and which gives, as he states, an ethylic salt with alcohol and hydrogen chloride.

An investigation of the rate of etherification of hydroxycarboxylic acids is in progress. The acids in all cases were dissolved in methylic alcohol and treated with hydrogen chloride during eight hours, the solution being maintained at the following temperatures:—0°, 20°, 40°, and the boiling point of methylic alcohol. Salicylic acid yields 9—10, 33—34, 81—82, and 98 per cent. of methylic salt respectively; hydroxynaphthalenecarboxylic acid [$COOH : OH = 1 : 2$] gives 0, 3, 26, and 63·5 per cent. respectively; the acid, [$COOH : OH = 2 : 3$], yields, at ordinary temperatures, 90 per cent. of methylic salt. Para-

hydroxybenzoic acid reacts as readily as benzoic acid, the meta-compound rather more slowly. If the solution of salicylic acid is not cooled, 50 per cent. of methylic salt is formed in eight hours. Methylic hydroxynaphthalenecarboxylate, [COOMe : OH = 1 : 2], dissolves in alkalis without colour, the 2 : 3 isomeric compound gives an intensely yellow solution. J. B. T.

Action of Sulphuric acid on Charcoal. By GIRAUD (*Bull. Soc. Chim.*, 1894, [3], **11**, 389—391).—During the preparation of sulphurous anhydride from charcoal and sulphuric acid, a white, crystalline sublimate occasionally forms in the neck of the flask, and may be obtained in quantity by using excess of charcoal and carrying on the action until gas ceases to be evolved. After purification and recrystallisation from alcohol, this substance forms small, colourless, efflorescent crystals, which, on sublimation, are transformed into a substance crystallising in long needles and melting at 280°. This forms a phthaleïn with phenol and sulphuric acid, and is probably pyromellitic anhydride, the original substance being the corresponding acid. Mellitic acid is possibly the first product. The substances are formed by the oxidation of some hydrogenated carbon compound, as neither coke nor recently ignited charcoal yield any crystals. Sugar and cellulose give a very poor yield, but ordinary coal yields as much as 5 per cent. JN. W.

Unsaturated Sulphones: Allylphenylsulphone and Allylparatolylsulphone. By ROBERT OTTO (*Annalen*, 1894, **283**, 181—208; compare Abstr., 1891, 1067 and 1229).—Allylphenylsulphone, $CH_2{:}CH{\cdot}CH_2{\cdot}SO_2Ph$, is obtained by heating the alcoholic solution of sodium benzenesulphinate in a reflux apparatus with allylic bromide (1 mol.) until the odour of the latter is no longer perceptible; it is a yellowish, odourless oil, which is heavier than water and is not miscible with it.

Allylparatolylsulphone is prepared in a similar manner from sodium paratoluenesulphinate; it melts at 52—53°, and forms crystals which belong to the monosymmetric system, $a : b : c = 1{\cdot}6955 : 1 : 0{\cdot}6671$. $\beta = 84°\ 51'$. Both sulphones are hydrolysed by alcoholic potash with formation of allylic alcohol and regeneration of the sulphinic acids from which they are derived; when reduced with zinc and hydrochloric acid, they give rise to the corresponding mercaptans.

αβ-Dibromopropylphenylsulphone is obtained by the action of bromine on phenylallylsulphone; it forms small plates which melt at 80°. *αβ-Dibromopropylparatolylsulphone* melts at 81—82°. On heating the former compound for several days with water at 110°, hydrogen bromide is eliminated with formation of *phenylsulphone-α-propylene glycol*, $CH_2(OH){\cdot}CH_2(OH){\cdot}CH_2{\cdot}SO_2Ph$, which crystallises in long, lustrous needles melting at 135—136°. The *dibenzoyl* derivative forms silky needles which melt at 86—87°; it is obtained by the action of benzoic chloride on the glycol, and also by heating a mixture of silver benzoate and *αβ*-dibromopropylphenylsulphone at 120° in benzene.

When the alcoholic solution of sodium benzenesulphinate is heated with dichlorhydrin for eight days, an oil is formed which contains a

small quantity of symmetrical diphenylsulphonisopropylic alcohol (compare Otto and Rössing, Abstr., 1890, 780).

Dibromopropylphenylsulphone does not yield allylphenylsulphone when heated with molecular silver; it is decomposed into potassium benzenesulphinate and propargylic alcohol by the action of alcoholic potash. On heating the alcoholic solution with sodium benzenesulphinate (2 mols.) for some days, *biphenylsulphonepropane*, $C_3H_6(SO_2Ph)_2$, is formed, a small quantity of allyltriphenyltrisulphone being produced at the same time (compare E. Stuffer, Abstr., 1890, 987). This substance melts at 101—102°, and is probably geometrically isomeric with trimethylenediphenyldisulphone and propylenediphenyldisulphone, which melt at 127—128° and 116° respectively.

Bitolylsulphonepropane, $C_3H_6(SO_2{\cdot}C_6H_4Me)_2$, is formed when dibromopropyltolylsulphone is heated with sodium paratoluenesulphinate, a small quantity of allyltritolyltrisulphone being also produced; it melts at 147—148°, and is isomeric with trimethyleneditolyldisulphone, which melts at 124—128°.

On heating a mixture of allylic tribromide and sodium benzenesulphinate in alcoholic solution, the corresponding trisulphone and a small quantity of biphenylsulphonepropane are formed. A similar reaction takes place between allylic tribromide and sodium paratoluenesulphinate.

αβ-Dithiophenylpropylphenylsulphone,

$$SPh{\cdot}CH_2{\cdot}CH(SPh){\cdot}CH_2{\cdot}SO_2Ph,$$

is obtained by heating the alcoholic solution of dibromopropylphenylsulphone with sodium phenylmercaptide on the water bath; it forms silky needles which melt at 75—77°. Oxidation with potassium permanganate converts it into allyltriphenyltrisulphone. On heating thiophenol (2 mols.) with epichlorhydrin, an oil is produced which yields the foregoing substance when heated with sodium benzenesulphinate; it therefore has the constitution $SPh{\cdot}CH_2{\cdot}CH(SPh){\cdot}CH_2Cl$.

M. O. F.

Iodo- and Iodoso-benzenesulphonic acids. By A. C. Langmuir (*Ber.*, 1895, **28**, 90—96).—Pariodobenzenesulphonic chloride yields a yellow, crystalline *iododichloride*, which melts and decomposes at 87—90°, reacts readily with potassium iodide, and is somewhat unstable; when treated with soda, it yields sodium pariodobenzenesulphonate. As the sulphonic chloride is less soluble than iodobenzenesulphonic acid, it was better suited for this investigation. *Metiodobenzenesulphonic acid*, prepared from metasulphanilic acid, is extremely soluble; the *sodium salt* crystallises with $1H_2O$ in colourless, lustrous plates. The *chloride*, $C_6H_4I{\cdot}SO_2Cl$, crystallises in long prisms, melting at 23°. The *sulphonamide* is deposited in lustrous needles or plates, and melts at 152°. The *iododichloride* resembles the para-compound; it melts and decomposes at 87°, and, with soda, yields sodium metiodobenzenesulphonate. The preparation of orthiodobenzenesulphonic acid is attended with great difficulty; it was converted into the chloride, and this into the *iododichloride*, $ICl_2{\cdot}C_6H_4{\cdot}SO_2Cl$, which is deposited in minute, pale yellow rhombohedra, and melts and decomposes at 65—67°. When acted on

by soda, it yields *sodium orthiodosobenzenesulphonate*, $IO{\cdot}C_6H_4{\cdot}SO_3Na$; it is a yellow, amorphous powder without smell, rapidly attacks potassium iodide solution in presence of acid, and yields iodobenzenesulphonic chloride by the action of phosphorus pentachloride.

The three iodobenzenesulphonic acids resemble the corresponding iodobenzoic acids in the conditions under which they yield iodoso-derivatives.

The benzenesulphonic chlorides are reduced to thiophenols by boiling with potassium iodide solution. J. B. T.

Dichloroxindenecarboxylic acid. By THEODOR ZINCKE and M. ENGELHARDT (*Annalen*, 1894, **283**, 341—360; compare Abstr., 1887, 54).—*β-Chloro-αα-ketoindenecarboxylic acid*, $C_6H_4<\begin{matrix}C(COOH)\\CO\end{matrix}>CCl$, is formed when dichloroxindenecarboxylic acid is heated with concentrated sulphuric acid at 100—110°. It crystallises in orange-red needles, and melts at 224°. The *methylic* salt forms brownish-yellow needles, which melt at 105°; the *ethylic* salt melts at 99—100°, and gives rise to an *oxime*, melting at 188°. The *oxime* of the acid crystallises in dark yellow needles; it melts at 256°, and yields an *acetyl* derivative, which melts at 218°. Alkalis convert the acid into a *compound*, $C_{20}H_{13}ClO_6$, which melts at 245°. When chloroketoindenecarboxylic acid is reduced with sodium amalgam, it gives rise to an *acid*, which forms a *silver* salt and an *acetyl* derivative. Hypochlorous and hypobromous acids convert chloroketoindenecarboxylic acid into dichlorodiketohydrindene- and chlorobromodiketohydrindene-carboxylic acids respectively. When acted on by chlorine, it yields tetrachloroketohydrindene, whilst *chlorodibromoketohydrindenecarboxylic acid*, $C_6H_4<\begin{matrix}CBr(COOH)\\CO\end{matrix}>CClBr$, is formed on treatment with bromine; this crystallises in white needles, and melts at 171°. The chlorobromo-derivative is decomposed by aqueous alkali, with formation of the *acid* $COOH{\cdot}C_6H_4{\cdot}C(CClBr){\cdot}COOH$, which crystallises from hot water in needles, and melts at 214°. The *barium* salt contains $1H_2O$, and the *silver* salt is amorphous; the *dimethylic* salt melts at 95°.

The *lactone*, $C_6H_4<\begin{matrix}C(OH)\\CCl\end{matrix}>\begin{matrix}CCl_2\\O\end{matrix}\!\!>CO$, is obtained by the action of chlorine on dichloroxindenecarboxylic acid. It forms lustrous prisms, which melt at 87°, and is readily converted into dichloroketoindene with elimination of hydrogen chloride and carbonic anhydride. Dichloroketoxyhydrindenecarboxylic acid is produced when the lactone is treated with aqueous sodium carbonate.

When the methylic salt of dichloroxindenecarboxylic acid is treated with chlorine, the methylic salt of tetrachloroxyhydrindenecarboxylic acid is formed; it melts at 166° (compare Zincke and Arust, Abstr., 1892, 858). M. O. F.

Synthesis of Indigo Blue. By CARL ENGLER (*Ber.*, 1895, **28**, 309—312).—Twenty-five years ago the author and A. Emmerling synthethised indigo by heating syrupy nitracetophenone with a

mixture of zinc dust and soda-lime. Wichelhaus' failure to obtain indigo in this manner was probably due to the presence of metanitracetophenone in considerable quantity in the nitro-product, to the temperature being too high, or to the use of unsuitable zinc dust.

The following method of obtaining indigo is trustworthy, and may be employed as a lecture experiment. Zinc dust (24 grams), soda-lime (4 grams), and recently ignited marble (2 grams) are intimately mixed, orthonitracetophenone (1 gram) dissolved in chloroform (10 vols.) is added, and, after thorough stirring, the mixture is exposed to the air for 1—2 days; portions of 1 gram are heated in a test-tube blown to a bulb, and placed horizontally over the blow-pipe for seven seconds, or somewhat longer over a burner. The reaction is facilitated by filling the tube with hydrogen and passing the evolved gases through water; the result is even better if, to the orthonitracetophenone, an equal amount of acetophenone is added, and the mixture treated with zinc dust, &c., as above. J. B. T.

Synthesis of Quinizarin and Hystazarin. By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 116—118).—When quinol dimethyl ether is heated with aluminium chloride and phthalic anhydride in presence of carbon bisulphide, 2 : 5-*dimethoxyorthobenzoylbenzoic acid* is formed. This crystallises in thick, white needles, melting at 162°, and by warming with concentrated sulphuric acid is converted into *quinizarin dimethyl ether*, $C_6H_4<^{CO}_{CO}>C_6H_2(OMe)_2$, which separates from alcohol in long needles, melting at 143°. From this compound, quinizarin can readily be obtained by hydrolysis with sulphuric acid.

Hystazarin may be prepared in a similar manner from veratroïl. 3 : 4-*Dimethoxyorthobenzoylbenzoic acid* forms white, lustrous plates, melting at 233°. *Hystazarin dimethyl ether* crystallises from acetic acid in golden-yellow needles. A. H.

Constitution of Isomeric Symmetrical Di-derivatives of Diphenylmethane and of Benzophenone. By WILHELM STAEDEL (*Annalen*, 1894, **283**, 149—151).—This paper contains a table setting forth the constitution of those dinitro-, diamido-, and dihydroxy-derivatives of diphenylmethane and of benzophenone, which are at present known. M. O. F.

Isomeric Dinitrodiphenylmethane Derivatives. By WILHELM STAEDEL (*Annalen*, 1894, **283**, 151—164; compare Abstr., 1894, i, 599).—Diphenylmethane when nitrated yields a mixture of 4 : 4′-dinitrodiphenylmethane, which melts at 183°, tetranitrodiphenylmethane, melting at 172°, and a small quantity of 2 : 4′-dinitrodiphenylmethane, which melts at 118°. After removal of these products, further nitration gives rise to *trinitrodiphenylmethane*, which melts at 109—110°; it is also obtained by heating diphenylmethane with fuming nitric acid (sp. gr., 1·53) for an hour at 50°.

4 : 4′-Diamidodiphenylmethane $CH_2(C_6H_4{\cdot}NH_2)_2$ (*α*), obtained by reducing the corresponding nitro-derivative with stannous chloride and hydrochloric acid, is identical with the base described by W. H.

Doer (this Journal, 1873, 170); it crystallises from hot water in lustrous plates, and melts at 85°. The *hydrochloride* and *sulphate* separate in well-formed crystals. The *diacetyl* derivative melts at 228°. The *diacetyl* derivative of 2 : 4′-diamidodiphenylmethane melts at 218—219°.

4 : 4′-Dihydroxydiphenylmethane is obtained from the amido-compound by means of the diazo-reaction; the *nitro*-derivative melts at 224°, and yields a *barium* salt, which separates in red crystals.

M. O. F.

Dinitro-, Diamido-, and Dihydroxy-Derivatives of Benzophenone. By WILHELM STAEDEL (*Annalen*, 1894, **283**, 164—180).—This paper contains an account of the production of dinitro- from mononitro-derivatives of benzophenone, a summary of the results having already appeared (Abstr., 1894, i, 599). The nitro-compounds give rise to the corresponding amido-derivatives on reduction.

4 : 2′-*Diamidobenzophenone* (δ) forms lustrous, straw-yellow needles, which melt at 128—129°; the *diacetyl* derivative crystallises in white plates, which melt at the same temperature, with evolution of gas. 2 : 3′-*Diamidobenzophenone* (ϵ) crystallises in golden-yellow plates, which melt at 80°; the *diacetyl* derivative is colourless, and melts at 167°. *Nitramidobenzophenone* is formed on reducing 2 : 3′-dinitrobenzophenone with tin and hydrochloric acid; it melts at 116°.

2 : 2′-Dihydroxybenzophenone is obtained from the amido-derivative by means of the diazo-reaction, xanthone being formed at the same time; it melts at 115°. 3 : 2′-Dihydroxybenzophenone is prepared in a similar manner; it forms white needles, which melt at 126°, instead of 121—122° as previously stated. A red, crystalline substance is also formed. The *acetyl* derivative of 3 : 2′-dihydroxybenzophenone melts at 154°.

2 : 4′-*Dihydroxybenzophenone* $OH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OH$ is identical with the substance obtained by A. Michael on heating a mixture of salicylic acid and phenol in presence of stannic chloride; the author has also prepared it from 2 : 4′-diamidobenzophenone by means of the diazo-reaction. It melts at 142°. The older method of preparation also gives rise to 4 : 4′-dihydroxybenzophenone, which melts at 210°. These two derivatives are formed when phenylic salicylate is heated with stannic chloride, but when phenylsalicylic acid is employed, the sole product is xanthone.

The dihydroxy-derivatives of benzophenone exhibit a certain regularity in their melting points.

M. O. F.

Hydroxydiphenylene Ketones and Hydroxydiphenylcarboxylic acids. By WILHELM STAEDEL (*Ber.*, 1895, **28**, 111—113; compare this vol., i, 147, and preceding page).—The substance obtained from symmetrical diorthodiamidobenzophenone by diazotising, and boiling with water the diazo-salt produced, is a *hydroxydiphenylene ketone*. It melts at 115°, is intensely yellow, and forms a wine-red solution in concentrated sulphuric acid. When its potassium salt is brought into fused potash, a carmine-coloured mass is first obtained, which soon becomes colourless. This contains the potassium salt of *orthophenylsalicylic acid*, [Ph : COOH : OH = 1 : 2 : 3], which crystallises from water in small prisms melting at

159°. It closely resembles salicylic acid in its properties, and, by treatment with strong sulphuric acid, is reconverted into the hydroxyphenylene ketone. Phenylbenzoic acid undergoes a similar reaction when dissolved in concentrated sulphuric acid.

The product obtained, in addition to symmetrical orthometadihydroxybenzophenone, from symmetrical orthometadiamidobenzophenone, is also probably a hydroxyphenylene ketone. By fusion with potash, it is converted into an acid, which is probably *orthophenylmetahydroxybenzoic acid*. Both the hydroxyphenylene ketones are coloured substances, and moreover act as dyes. A. H.

Constitution of the Triphenylmethane Colour-bases. By Hugo Weil (*Ber.*, 1895, **28**, 205—215).—Reasons are given for supposing that compounds such as pararosaniline have the constitution $(NH_2\cdot C_6H_4)_2C<^{-O-}_{C_6H_4}>NH_3$, rather than $(NH_2\cdot C_6H_4)_3C\cdot OH$, which is usually assigned to them, although they are stronger bases than the leuco-compounds, from which they are supposed to be derived by the displacement of H by OH, a change which should *lessen* the basic properties. In the first place, only *two* amido-groups in rosaniline react with paranitrobenzaldehyde, *dinitrodibenzylidenerosaniline*, $C_{34}H_{27}N_5O_5$, being formed, a yellow, crystalline substance melting at 235°; the same compound appears to be formed when rosaniline acetate is used. If, however, hydrocyanorosaniline, in which the CN group is known to be united to carbon, is used, a *trinitrotribenzylidenerosaniline* compound, $C_{42}H_{29}N_7O_6$, is formed; this is a yellow, crystalline powder, and melts at 144—145°. Secondly, the oxygen atom does not react like hydroxyl oxygen, but rather resembles that in ethylenic oxide and epichlorhydrin. Malachite green, $NMe_2\cdot C_6H_4\cdot CPh<^{-O-}_{C_6H_4}>NHMe_2$, yields a colourless *oxime* and a yellowish *phenylhydrazone*, which melt and decompose at 168° and 167° respectively. And, lastly, malachite green, when heated at 200°, behaves very like tetramethylammonium hydroxide; it loses, not methylic alcohol, indeed, but formaldehyde, and there remains a brownish substance which melts at 155—156°, and may be either $NMe_2\cdot C_6H_4\cdot CHPh\cdot C_6H_4\cdot NHMe$ or $NMe_2\cdot C_6H_4\cdot CPh{:}C_6H_4{:}NH_2Me$.

Attention is called to the fact that the new formula allows of two isomeric rosanilines, $(NH_2\cdot C_6H_4)_2C<^{-O-}_{C_7H_6}>NH_3$ and

$$\begin{matrix}NH_2\cdot C_6H_4\\NH_2\cdot C_7H_6\end{matrix}>C<^{-O-}_{C_6H_4}>NH_3.$$

C. F. B.

Constitution of Fluoresceïn and Eosin. By Gustav Heller (*Ber.*, 1895, **28**, 312—316).—Graebe's failure to obtain anthraquinone derivatives from dihydroxyorthobenzoylbenzoic acid or its ethereal salts has led him to suggest that the hydroxyl groups are not in the para-position relatively to the methane carbon atom, and that fluoresceïn is represented by the formula

$$CO<^{C_6H_4}_{O\ \ -}>C<^{C_6H_3(OH)}_{C_6H_3(OH)}>O$$

[C : OH : O = 1 : 2 : 6]; the generally accepted constitution is [C : OH : O = 1 : 4 : 6] (compare this vol., i, 182). The author has also failed to obtain an anthraquinone derivative from hydroxyorthobenzoylbenzoic acid [CO : OH = 1 : 4] (Abstr., 1893, i, 274), whilst Nourisson prepared hydroxyanthraquinone from the corresponding methoxy-derivative. The reason for this difference is that in the former case a sulphonic acid is formed which is incapable of condensation; in the latter, the methoxyanthraquinone which is first produced is immediately hydrolysed. Dihydroxyorthobenzoylbenzoic acid yields a dibromo-derivative which is identical with Baeyer's "dibromomonoresorcinolphthaleïn," prepared by the action of soda on eosin; when heated with fuming sulphuric acid, it is converted into dibromodihydroxyanthraquinone [OH : Br : OH : Br = 1 : 2 : 3 : 4], Plath's "dibromoxanthopurpurin;" dibromodihydroxyorthobenzoylbenzoic acid must therefore have the constitution

[CO : OH : Br : OH : Br = 1 : 2 : 3 : 4 : 5],

since one of the hydroxyl groups (oxygen atom) in fluoresceïn is certainly in the ortho-position to the methane carbon atom. The position of the bromine atoms in eosin is also determined, since both in this compound and in fluoresceïn the resorcinol radicles are symmetrical.

Hydroxyorthobenzoylbenzoic acid also yields a dibromo-derivative which condenses in a manner similar to the dihydroxy-compound, forming the dibromhydroxyanthraquinone which Baeyer prepared by heating tetrabromophenolphthaleïn with concentrated sulphuric acid (Abstr., 1880, 654). J. B. T.

Nitronaphthalenes. By Wilhelm Will (*Ber.*, 1895, **28**, 367—379).—The substance melting at 212°, described by de Aguiar, and afterwards by Beilstein and Kuhlberg (*Annalen*, **169**, 99), as α-tetranitronaphthalene, is a mixture of two compounds, which may be separated by treatment with cold acetone. *γ-Tetranitronaphthalene* is readily soluble in acetone, and crystallises in pale yellow, lustrous tetrahedra melting at 194—195°. It dissolves without decomposition in concentrated nitric or sulphuric acid, but is decomposed by alkalis. When treated with phosphorus iodide and water, it is converted into the crystalline *hydriodide of γ-tetramidonaphthalene*, from which the free base has not as yet been prepared. When the nitro-compound is suspended in methylic alcohol and treated with a solution of sodium methoxide, *methylic γ-trinitronaphthylic ether*, $C_{10}H_4(NO_2)_3{\cdot}OMe$, is formed. This substance crystallises in golden-yellow needles, and melts at 186°. γ-Tetranitronaphthalene is converted by oxidation with dilute nitric acid or sodium peroxide into paradinitrophthalic acid, melting at 201° [NO_2 : COOH : COOH : NO_2 = 1 : 2 : 3 : 4]. The trinitronaphthylic ether, on the other hand, is not oxidised by sodium peroxide, but is converted by nitric acid into metadinitrophthalic acid, melting at 226° [NO_2 : COOH : COOH : NO_2 = 1 : 2 : 3 : 5]. The γ-compound is therefore a 1 : 3 : 1′ : 4′-tetranitronaphthalene, and the substitution of methoxyl for the nitro-group takes place in agreement with the observations of Lobry

de Bruyn, according to which ortho- and para-nitro-groups are readily displaced, whilst meta-groups are not.

δ-Tetranitronaphthalene is insoluble in acetone and all the usual solvents. It may be recrystallised from boiling ethylic benzoate or concentrated nitric acid, and forms slender needles or compact prisms which begin to decompose at 270°, but do not melt even at 310°. Like the γ-compound, it can be reduced to a *tetramido-compound*, of which the *hydriodide* is a crystalline substance, easily decomposed by a large amount of water. The free base has not yet been isolated. *δ-Trinitronaphthylic methylic ether* crystallises in yellow needles melting at 191°. On oxidation with sodium peroxide, the δ-tetranitro-compound yields paradinitrophthalic acid (m. p. 201°), whilst with nitric acid it gives an acid which is most probably paradinitrobenzoic acid. The trinitronaphthylic ether also yields paradinitrophthalic acid when treated with nitric acid. Since the δ-compound is obtained by the nitration of 1 : 4′-dinitronaphthalene, it follows from the result of the above oxidation experiments that three of the nitro-groups must have the positions 1 : 4 : 4′. The position of the fourth follows from the constitution of the trinitronaphthalene, from which it can be prepared. Two trinitronaphthalenes derived from α-dinitronaphthalene have hitherto been described. A third, *δ-trinitronaphthalene*, is formed, along with the α-trinitro-compound, when α-dinitronaphthalene is heated with a large amount of nitric acid of sp. gr. 1·42. It crystallises from alcohol in slender, colourless needles melting at 112—113°.

γ-Trinitronaphthalene, melting at 154°, is converted by oxidation with nitric acid into paranitrophthalic acid, and with sodium peroxide into orthomononitrophthalic acid. It therefore has the constitution 1 : 4 : 4′. Fuming nitric acid and sulphuric acid convert it into a mixture of the γ- and δ-tetranitro-compounds. α-Trinitronaphthalene, on oxidation with sodium peroxide, yields orthomononitrophthalic acid, whilst on further nitration, it only gives the γ-tetranitro-compound.

The new δ-trinitronaphthalene yields, on nitration, the δ-tetranitro-compound, accompanied by another substance which has not been examined.

Since γ-tetranitronaphthalene (1 : 3 : 1′ : 4′) can only be obtained by the nitration of the trinitronaphthalenes 1 : 4 : 4′ and 1 : 3 : 4′ (both derived from 1 : 4′-dinitronaphthalene), and since γ-trinitronaphthalene has been shown to have the constitution 1 : 4 : 4′, it follows that α-trinitronaphthalene has the constitution 1 : 3 : 4′. δ-Trinitronaphthalene must therefore be the 1 : 2 : 4′-compound, since 1 : 4′-dinitronaphthalene can only yield these three trinitro-derivatives. δ-Tetranitronaphthalene, being formed by the nitration of both the γ- and the δ-trinitro-compounds, must therefore have the constitution 1 : 2 : 1′ : 4′.

γ- and δ-tetranitronaphthalene are formed in about equal amounts by the nitration of dinitronaphthalene, and are accompanied by paradinitrophthalic acid and another substance, melting at 200°, which has not been further examined.

β-Dinitronaphthalene [1 : 1′] on nitration appears to yield only

one derivative, β-tetranitronaphthalene, a certain amount of meta-dinitrophthalic acid being also formed. This substance does not react with sodium methoxide, and is therefore probably the 1 : 3 : 1′ : 3′-compound. A. H.

Thio-derivatives of β-Naphthol. By ROBERT HENRIQUES (*Ber.*, 1895, **28**, 114).—The author admits the identity of the substances previously described by him with those first prepared by Schiller-Wechsler (this vol., i, 150). The melting point of dehydrodihydroxydinaphthylic sulphide (thiodinaphthylic oxide) is 155° and not 159—160° as stated by Schiller-Wechsler. A. H.

Derivatives of Iodohydroxynaphthaquinone (Iodonaphthalic acid). By FRIEDRICH KEHRMANN and B. MASCIONI (*Ber.*, 1895, **28**, 345—352).—Iodohydroxy-α-naphthaquinone is prepared by treating hydroxynaphthaquinone, dissolved in acetic acid, with sodium iodide and iodate in presence of sulphuric acid. It crystallises in thick, yellowish-brown, lustrous prisms, is almost insoluble in water, and melts and decomposes at above 170°. The alkali solutions are blood-red, and the *sodium* salt crystallises in dark red masses. The *silver* salt is a dark red, crystalline powder. The *methylic ether*, melting at 156—157°, and the *ethylic ether*, melting at 128—129°, form pale yellow needles. The silver salt is completely decomposed by water or dilute ammonia at 120°, no hydroxy- or amido-derivative being formed. Stannous chloride reduces the iodoquinone to 1 : 2 : 4-trihydroxynaphthalene, which is at once converted by the oxygen of the air into hydroxynaphthaquinone. The methylic ether, on reduction, yields colourless plates of *dihydroxymethoxyiodonaphthaquinone*, which cannot be isolated in the pure state. The corresponding *diacetate*, $C_{10}H_4(OAc)_2(OMe)I$, crystallises in thick, colourless prisms melting at 162—163°. *Iodamidonaphthaquinone*, $C_{10}H_4O_2(NH_2)I$, is obtained by the action of alcoholic ammonia on the methylic ether, and forms dark red needles melting at 192—193°. On reduction, it yields 2-amido-1 : 4-naphthaquinone, identical with that described by Meerson (Abstr., 1888, 713, 1200). This method of preparation affords an independent proof of the constitution of the base. Iodohydroxynaphthaquinone combines with aniline to form a salt, which is at once decomposed by hydrochloric acid, but when heated with aniline in alcoholic solution it yields anilido-α-naphthaquinone. With orthophenylenediamine it yields α-naphthoeurhodole, a portion of the diamine being also oxidised to diamidophenazine. Phenylphenylenediamine reacts in a similar manner, rosindone and the hydriodide of the oxidation product of the amine, which has been described by Fischer and Heiler (Abstr., 1893, i, 266) being formed.

Hydroxyiodonaphthaquinonoxime crystallises with $2H_2O$ in yellow prisms, which lose their water at 100° and decompose at 160° without melting. When reduced with stannous chloride, the oxime is converted into 1 : 2 : 4-*amidodihydroxynaphthalene*, the hydrochloride of which is precipitated by hydrochloric acid from aqueous solution in colourless crystals. Ferric chloride converts it into hydroxynaphthaquinone. The neutralised solution, when exposed to atmo-

spheric oxygen, yields naphthoresorufin (compare this vol., i, 246), whilst a strongly alkaline solution is thereby converted into hydroxynaphthaquinone.

When the hydrochloride is treated with sodium acetate and acetic anhydride, the *triacetyl-derivative* is obtained in thick tablets melting at 155—156°. The base just described is identical with the product of reduction of hydroxynaphthoquinonoxime, and, since 1 : 3 : 4-amidodihydroxynaphthalene and 2 : 1 : 4-amidodihydroxynaphthalene are already known, must have the constitution of a 1 : 2 : 4-amidodihydroxynaphthalene, only these three isomerides, having the three groups in the positions 1 : 2 : 4, being possible. It hence follows that, by the action of alkaline hydroxylamine on hydroxynaphthaquinone and its iodo-derivative, the oxygen atom adjacent to the hydroxyl group is displaced. A. H.

Azo-derivatives of Phenyl-β-naphthylamine. By THEODOR ZINCKE (*Ber.*, 1895, **28**, 328—333).—A general account is given of the ammonium base derived from benzenazo-β-naphthylphenylamine (Abstr., 1890, 990); the constitution of both compounds is discussed; and they are compared with the formazyl and tetrazolium derivatives respectively. Marshall's work is also summarised (following abstract). J. B. T.

Anilido- and Paratolylamido-β-naphthaleneazobenzoic acids and their Oxidation Products. By J. W. MARSHALL (*Ber.*, 1895, **28**, 333—340).—*Anilido-β-naphthaleneparazobenzoic acid*,

$$NHPh\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot COOH \text{ or } NHPh\cdot N{:}C_{10}H_6{:}N\cdot C_6H_4\cdot COOH,$$

like its isomerides, is prepared from phenyl-β-naphthylamine and diazobenzoic acid chloride in a manner similar to the benzene-derivative (Abstr., 1887, 731). It is purified by means of the sodium salt, crystallises from glacial acetic acid in dark red, metallic, lustrous needles, and melts at 258°. The *sodium salt* crystallises in deep red plates, and is sparingly soluble in water. The *calcium* and *barium salts* and also those of the heavy metals are red to reddish-brown, and almost insoluble in water.

Anilido-β-naphthalenemetazobenzoic acid crystallises in light red, lustrous needles, and melts at 235°. The *sodium salt* is deposited in light red plates; like the other salts, it resembles the para-compound.

Anilido-β-naphthaleneorthazobenzoic acid, like its salts, is more readily soluble than the meta- and para-compounds, it crystallises in red needles, and melts at 215°.

Paratolylamido-β-naphthaleneparazobenzoic acid,

$$C_6H_4Me\cdot NH\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot COOH,$$

prepared like the phenyl derivative, forms small, dark red, crystalline granules or needles, is very sparingly soluble, and melts at 262°. The *sodium salt* crystallises in dark red, metallic, lustrous plates, and dissolves with difficulty. The salts of the other metals are insoluble

and red to brownish-red. The corresponding *meta-* and *ortho-acids* crystallise in red needles, resemble the phenyl derivatives, and melt at 245° and 221° respectively. The salts resemble those of the phenyl compounds. The above azo-compounds are all readily resolved into benzonaphthazine and tolunaphthazine when boiled with glacial acetic acid and a little hydrochloric acid. By the action of bromine in glacial acetic acid solution, bromobenzoic acids and tetrabromophenyl- or tetrabromotolyl-β-naphthylamine are formed; the latter compound crystallises in slender, lustrous needles, and melts at 168°. The action of chlorine has only been studied in the case of anilido-β-naphthaleneparazobenzoic acid, which yields diazobenzoic acid chloride and chloronaphthylphenylamine, the former only was isolated. The three benzoic acid phenyl compounds when oxidised yield ammonium bases, $C_{10}H_6<\begin{matrix}N\\|\\N(OH)Ph\end{matrix}\!\!>\!N\cdot C_6H_4\cdot COOH$ or

$$C_{10}H_6\ll\begin{matrix}N\\|\\N(OH)Ph\end{matrix}\!\!>N\cdot C_6H_4\cdot COOH,$$

which easily form betaïnes, $C_{10}H_6<\begin{matrix}N\\|\\NPh\end{matrix}\!\!>\!N\cdot C_6H_4\!>\!CO$; these have an extremely bitter taste, become red on treatment with soda, regenerate the diazo-compounds when reduced, decompose when heated alone, and do not affect litmus paper. The *parabetaïne* crystallises with $3H_2O$ in highly lustrous prisms; its *chloride*, $C_{23}H_{16}N_3O_2Cl$, is deposited in pale yellow needles or plates, the *sulphate* in pale yellow, the *nitrate* in colourless needles. The *metabetaïne* crystallises with $3H_2O$ in thick, highly lustrous, yellowish needles; its *chloride* and *nitrate* are deposited in pale yellow needles. The *orthobetaïne* is deposited in small, lustrous, monoclinic prisms with $2H_2O$. The salts crystallise with difficulty, the *chloride* in small plates, the *nitrate* in granules, and the *sulphate* in needles. All three betaïnes form *platinochlorides* which are yellow, and *mercurochlorides* which are white.

J. B. T.

Derivatives of Naphthalic acid. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 360—364).—The author has investigated a number of alkyl substitution products and other derivatives of naphthalimide. The *potassium* salt of naphthalimide, $C_{10}H_6{:}(CO)_2{:}NK$, crystallises in small, colourless needles, and the *sodium* salt closely resembles it. *Methylnaphthalimide* may be prepared by acting on the potassium salt with methylic iodide or by acting on naphthalic anhydride with methylamine. It forms small, white needles melting at 205°. *Ethylnaphthalimide* also forms small needles, and melts at 148°. *Phenylnaphthalimide* (naphthalanil), obtained by the direct action of aniline, also crystallises in small needles, and melts at 202°. *Orthotolylnaphthalimide* melts at 214·2°. *Benzylnaphthalimide* melts at 196·6°. *Naphthaloxime* (naphthalhydroxamic acid), $C_{10}H_6{:}(CO)_2{:}N\cdot OH$, is prepared by the action of hydroxylamine in alkaline solution on the anhydride. It forms a white, matted, crystalline mass, and melts at 284°. It readily forms metallic salts which are coloured red, the *potassium*, *sodium*, and *silver* salts having been analysed. *Methyl-*

naphthaloxime, like the oxime itself, is colourless, and melts at 212°. *Ethylnaphthaloxime* forms small needles melting at 160°. *Naphthalphenylhydrazone*, $C_{10}H_6(CO)_2{:}N{\cdot}NHPh$, is obtained by the direct action of phenylhydrazine on the anhydride at 170°; it crystallises in compact prisms melting at 218·5°. Acetic chloride converts it into the *acetyl* derivative, which forms small, white plates, and melts at 230°.

Benzoylnaphthalphenylhydrazone crystallises in small needles, and melts at 235°. Naphthalphenylhydrazone is converted, by reduction, into a substance which is apparently the *hydrazone* of *hydroxynaphthalide*, $C_{10}H_6<\begin{matrix}C(OH)H\\CO\end{matrix}>N{\cdot}NHPh$, since, on distillation, it decomposes into naphthalimide and aniline. A. H.

Campholenes and the Constitution of Camphor. By Auguste Béhal (*Compt. rend.*, 1894, **119**, 858—862).—The campholene obtained by the action of heat on the campholenic acid previously described (next page) boils at 135·5° under a pressure of 755 mm., is optically inactive, and has an odour of terebenthene; sp. gr. at 0° = 0·8134. It combines with hydrogen iodide with development of heat, and the crystalline compound formed melts at about 61°; this is very unstable, losing hydrogen iodide gradually when exposed to the air, and instantly in presence of water. When treated with an alkali, it yields *isocampholene*, an isomeride of the original hydrocarbon, which boils at 134°; sp. gr. at 0° = 0·8117. Isocampholene yields the original compound with hydrogen iodide, and is identical with the campholene obtained by Guerbet from campholic acid.

The existence of two campholenes throws some light on the position of the ethylene linking in campholene. The action of bromine on campholene and isocampholene in presence of dry chloroform gave no definite results, 4 atoms of bromine being taken up. Nitrosyl chloride, on the other hand, yields a blue crystalline product with isocampholene, but not with campholene, and hence it would seem that in isocampholene the ethylene linking is in the nucleus and in campholene in the side chain. This view agrees with the behaviour of the hydriodide and the formation of isocampholene from the hydriodide produced by the campholene.

It is probable that in campholenic acid the carboxylic group is attached to the methylene group. This view is supported by the ready decomposition of the acid, the formation of a lactone boiling at 255° under a pressure of 760 mm., and the general chemical behaviour of camphor, which in the author's opinion has the constitution represented by Bouveault's formula. C. H. B.

Campholic acid. By Guerbet (*Bull. Soc. Chim.*, 1894, [3], **11**, 426—433).—An improved method of preparing campholic acid is to heat camphor (500 grams) with sodium (40 grams) in xylene solution (500 c.c.), first at ordinary temperatures until the sodium has dissolved, and then, after removal of the solvent, &c., under low pressure in closed vessels for 24 hours at 280—290°. The portion of the product soluble in water is neutralised with hydrochloric acid, and

the campholic acid precipitated by carbonic anhydride; after recrystallisation from alcohol it is pure.

Montgolfier's explanation of the mechanism of the action is incorrect, as the terpene, assumed by him to be formed, could not be detected.

Campholic acid is reduced by hydriodic acid to mesitylene, hexahydromesitylene, and pseudocumene. Hexahydromesitylene yields trinitromesitylene when nitrated in the usual manner. JN. W.

Campholenic acids and Campholenamides. By AUGUSTE BÉHAL (*Compt. rend.*, 1894, **119**, 799—802).—When campholenonitrile, obtained by the action of acetic chloride on camphoroxime, and boiling at 222°, is boiled for about 20 minutes with alcoholic potash, it yields campholenamide, which crystallises from water or alcohol in silky needles melting at 83°. The melting point of this amide is generally stated to be between 124° and 127°.

When the amide is boiled for a long time with alcoholic potash, it yields campholenic acid, which is colourless, odourless, and tasteless, melts at 50°, and boils at 185° under a pressure of 120 mm. When quite pure, it also boils without change at 247—248° under normal pressure, but in presence of a trace of alkali it completely decomposes into campholene and carbonic anhydride.

Although only slightly soluble in water, this campholenic acid is acid to litmus, and decomposes carbonates; its amide is hydrolysed without difficulty; when treated with hydrochloric acid and alcohol, it yields an ethylic salt which boils at 225°, and is rapidly hydrolysed by alcoholic potash, regenerating the original acid. These facts and the loss of carbonic anhydride on distillation all go to prove the existence of a true acid function. The acid also contains ethylenic carbon, for, when treated with hydrogen iodide in presence of light petroleum, it yields a crystalline acid which melts at 66° and decomposes in moist air, with liberation of hydrogen iodide and formation of an acid which is not identical with the original acid.

Campholenonitrile, dissolved in benzene, combines with hydrogen iodide with development of heat and formation of a white compound which melts at about 84°. It follows that the rupture of the camphor nucleus takes place at the moment of formation of the nitrile. This rupture can be brought about by most dehydrating agents. The compound of the nitrile with hydrogen iodide loses the latter more slowly under the influence of moist air and alkalis than the analogous compound formed by campholenic acid, and the nitrile formed is not identical with the original nitrile, although it has a similar odour and boils at nearly the same temperature. The former is slowly acted on by alcoholic potash, and yields an amide melting at 92°, whilst the former is rapidly attacked, and the amide melts at 83°.

Both amides have, however, very similar properties; they are only slightly soluble in water, and crystallise in needles very soluble in strong alcohol, but only slightly so in dilute alcohol of 40°. They are very soluble in hot, light petroleum, but only slightly in the cold.

It would seem that there are at least three distinct campholenic acids, the amides of which melt at 83°, 92°, and 127° respectively.

C. H. B.

Camphoronic acid: a Correction. By OSSIAN ASCHAN (*Ber.*, 1895, **28**, 224).—It was erroneously stated (this vol., i, 188) that the barium salt of *i*-camphoronic acid, unlike the two isomeric salts, is soluble in water. It is of the *calcium* salt that this is true; the barium salts of all three isomeric acids are only sparingly soluble in water. C. F. B.

Camphoronic acid. By JULIUS BREDT (*Ber.*, 1895, **28**, 316—321).—*Anhydrocamphoronic chloride*, $O:(CO)_2:C_6H_{11}\cdot COCl$, exists in two modifications; the α-compound (m. p. 131°) has been described by Kachler; it boils at 164—165° (13 mm.), and is then almost entirely converted into the β-compound which forms rhombic crystals, melts at 38—39°, and boils at 151° (10 mm.). *Methylic camphoronate*, $C_6H_{11}(COOMe)_3$, boils at 155° (12 mm.). The *dimethylic salt* is formed together with the preceding compound, or from the anhydro-chloride. *Methylic anhydrocamphoronate*,

$$O:(CO)_2:C_6H_{11}\cdot COOMe,$$

prepared by submitting the preceding compound to distillation, or from the anhydro-chloride, exists in two isomeric forms. The α-compound is deposited in rhombic crystals, melts at 138°, and boils at 166—167° (12 mm.). The β-derivative forms similar crystals, is more soluble, melts at 45°, and boils at 156° (10 mm.). *Methylic dihydrogen camphoronate*, $C_6H_{11}(COOH)_2\cdot COOMe$, obtained by the action of water on the preceding compound at ordinary temperatures, crystallises in needles melting at 125—126°.

Anhydrocamphoronic anilide, $O:(CO)_2:C_6H_{11}\cdot CO\cdot NHPh$, is prepared from either of the anhydro-chlorides; it is crystalline and melts at 202—203°.

Bromanhydrocamphoronic chloride, $O:(CO)_2:C_6H_{10}Br\cdot COCl$, formed by the interaction of bromine and either of the anhydrochlorides at 120°, is deposited from ether in monoclinic crystals, melts at 168°, and, when boiled with water, is converted into Kachler's "α-hydroxycamphoronic acid;" no β-compound could be detected. A second bromochloride is formed with the preceding compound, but on account of its ready solubility it could not be isolated; with water, it yields both α- and β-hydroxycamphoronic acid. *Bromanhydrocamphoronic acid*, $O:(CO)_2:C_6H_{10}Br\cdot COOH$, is prepared from the corresponding chloride (m. p. 168°) by the action of glacial acetic acid; it is crystalline, and melts at 154°. A *methylic salt*, $O:(CO)_2:C_6H_{10}Br\cdot COOMe$, is formed on boiling the bromochloride with methylic alcohol and rapidly cooling the solution; it is deposited in lustrous plates and in rhombic crystals, melts at 100°, and boils at 177° (15 mm.). By the action of hydrogen chloride in methylic alcoholic solution, an isomeric salt is formed which is deposited in rhombic crystals, melts at 142°, and, when boiled under reduced pressure, is resolved into methylic bromide, and Kachler's "α-hydroxycamphoronic anhydride;" it behaves, therefore, like a γ-bromo-ethylic salt. "α-Hydroxycamphoronic acid," $\begin{matrix}O\\|\\CO\end{matrix}>C_6H_{10}\cdot(COOH)_2$, is dibasic, and bears the same relationship to bromanhydrocamphoronic acid that camphanic acid,

$$\begin{matrix}O-\\ |\\ CO\end{matrix}>C_6H_{13}\cdot COOH,$$

does to bromocamphoric anhydride, $C_8H_{13}Br{:}(CO)_2{:}O$; it is the lactone of the β-hydroxy acid, and is formed from bromanhydrocamphoronic acid (see above) and water; the author suggests for it the name *camphoranic acid*. "β-Hydroxycamphoronic acid," $OH\cdot C_6H_{10}\cdot(COOH)_3$, is tribasic; it may be converted into the lactone, and, when distilled, yields *camphoranic anhydride*,

$$\begin{matrix}O-\\ |\\ CO\end{matrix}>C_6H_{10}<\begin{matrix}CO\\ CO\end{matrix}>O,$$

which melts at 136—137°, and boils at 175° (10 mm.). *Dimethylic camphoranate*, $\begin{matrix}O-\\ |\\ CO\end{matrix}>C_6H_{10}(COOMe)_2$, is deposited from water in long needles, from methylic alcohol in rhombic crystals, melts at 111°, and is formed in small quantity from methylic alcohol and bromanhydrocamphoronic chloride. The *methylic hydrogen salt*, formed together with the preceding compound, is deposited from water in rhombic sphenoidal crystals with $1H_2O$ and melts at 81—83°. The anhydrous compound melts at 183°, and is deposited from ether in tetragonal crystals. Most of the preceding compounds have been examined crystallographically; an account of the results, together with certain theoretical conclusions, will be given later. J. B. T.

Some Points in Stereochemistry. By Louis Bouveault (*Bull. Soc. Chim.*, 1894, [3], **11**, 356—359).—A rejoinder to Combes (this vol., i, 108). The author maintains that it is possible for the four valencies of a carbon atom to exist in one plane, and that, moreover, when three of the valencies are in one plane, as in the central carbon atom of the author's formula for terebenthene, the fourth is necessarily also in the same plane. Jn. W.

Stereochemistry. By Alphonse Combes (*Bull. Soc. Chim.*, 1894, [3], **11**, 436—439).—A reply to Bouveault (preceding abstract). Jn. W.

Essence of Ylang-ylang. By Albert Reychler (*Bull. Soc. Chim.*, 1894, [3], **11**, 407—412).—There are two varieties of this essence, *oleum Anonæ odoratissimæ* and *oleum Canangæ;* the present paper refers to the former; this, when distilled under reduced pressure, is resolved chiefly into two fractions, the one boiling at 100—112°, the other at 130—146°.

The more volatile fraction is hydrolysed by alcoholic potash into benzoic acid and a phenol on the one hand, and an unsaturated isomeride of geraniol on the other. *Ylangol*, $C_{10}H_{18}O$, the isomeride of geraniol (molecular weight by cryoscopic method), boils under 28 mm. pressure at 103—107°; the sp. gr. = 0·886 at 15°; the sp. rotatory power in alcoholic solution $[\alpha]_D = -20·7°$. The refractive index at 15·5° is $[\mu]_D = 1·472$, and the molecular refractive power therefore 48·64, a number pointing to the presence of two ethylene linkings in the molecule, and confirmed by the relative amount of iodine absorbed. Ylangol

is oxidised by chromic mixture to an aldehydic substance, probably citral.

The fraction boiling at 130—146° consists probably of a sesquiterpene. The author is proceeding with the study of the Cananga essence. JN. W.

Constitution of Ring Systems. By WILLY MARCKWALD (*Ber.*, 1895, **28**, 114—116; compare Abstr., 1894, ii, 474).—The author defends the conclusions as to the effect of reduction on the properties of various ring-compounds, given in his previous papers, against the criticism to which they have been subjected by Bamberger (*Ber.*, **27**, 3427). A. H.

Quinoline Bases in Brown Coal-tar. By OSCAR G. DOEBNER (*Ber.*, 1895, **28**, 106—107).—The fraction of brown coal-tar which boils between 220—280° contains quinoline and some of its homologues. The quinoline may be isolated by the recrystallisation of the picrates prepared from the redistilled fractions of this portion of the oil. The homologues have not yet been individually separated. A. H.

Derivatives of α-Quinoquinoline. By ARNOLD REISSERT (*Ber.*, 1895, **28**, 119—129).—The name quinoquinoline is ascribed to a (hypothetical) compound of the formula $\begin{matrix}CH{:}CH{\cdot}C{\cdot}CH\\ \|\quad\quad\|\quad\ |\\ CH{:}N{-}C{\cdot}N{-}\end{matrix}\!>C_6H_4$.

Methyl chloronicotinate COOMe : Cl = 3 : 6 is prepared by acting with phosphorus pentachloride on the corresponding hydroxy-acid, and pouring the liquid thus obtained into methylic alcohol. It forms stellate groups of broad, lustrous needles and melts at 86—89°. It has a strong odour of fennel. *Ethoxynicotinic acid*, [COOH : OEt = 3 : 6], is prepared by boiling chloronicotinic acid or its methylic salt with alcoholic soda. It forms small crystals melting at 183°.

Methylic chloronicotinate readily undergoes condensation with anthranilic acid when the two are heated together at 170°. The product consists of *methylic α-quinoquinolone-β-carboxylate*,

$$COOMe{\cdot}C_5NH_2\!<\!\begin{matrix}CO\\ NH\end{matrix}\!>C_6H_4,$$

which crystallises in clusters of small, bright yellow needles, melting at 176°. It dissolves readily in mineral acids, forming salts which are not decomposed by water. Aqueous alkalis convert it into the acid, which can also be obtained by the direct condensation of the chloronicotinic acid with anthranilic acid. *α-Quinoquinolone-β-carboxylic acid* crystallises in small, soft, pale yellow needles, which melt and decompose at 318—319°. The freshly precipitated acid readily dissolves in mineral acids, whereas the crystalline acid only dissolves very slowly. The crystalline *barium* salt has the composition

$$(C_{13}H_7N_2O_3)_2Ba + 4H_2O.$$

The product of the direct condensation of chloronicotinic acid with anthranilic acid contains, in addition to the acid just described, a

compound which is probably *α-quinoquinolone-β-carboxyorthocarboxyanilide*, $COOH\cdot C_6H_4\cdot NH\cdot CO\cdot C_5NH_2<^{CO}_{NH}>C_6H_4$.

This substance is sparingly soluble in cold ammonia and is precipitated by acids as a yellow, non-crystalline mass, which is almost insoluble in the usual solvents, but dissolves in concentrated nitric or sulphuric acid and is re-precipitated by the addition of water. It melts at 336°. When boiled with aqueous soda, it is converted into anthranilic acid and quinoquinolonecarboxylic acid.

α-Quinoquinolone, $C_5NH_3<^{CO}_{NH}>C_6H_4$, is formed when quinoquinolonecarboxylic acid is heated above its melting point. It crystallises in light yellow, lustrous needles, melting at 210°, and has strongly marked basic properties. Mineral acids dissolve it to form solutions which have a strong blue fluorescence. The *hydrochloride* forms light yellow needles melting at 292—293°. The *platinochloride* melts at 248°, the *aurochloride* at 236° and the *picrate* at 238°. Quinoquinolone is not affected by distillation over heated zinc dust, by treatment with phosphorus pentachloride or by the action of sodium amalgam on its alcoholic solution. Hydriodic acid at 220—230° converts it into a substance which crystallises in colourless, lustrous plates or broad needles, and melts at 160°; this is probably *dibenzoyloctohydro-α-quinoquinoline*, $C_5NH_8Bz<^{CH_2}_{NBz}>C_6H_4$.

A. H.

Oxazines of the Naphthalene Series. By Friedrich Kehrmann (*Ber.*, 1895, **28**, 353—359; compare Abstr., 1894, i, 54).—*Naphthophenoxazone*, $C_{10}H_5O<^{N}_{O}>C_6H_4$, is formed when orthamidophenol is heated with hydroxynaphthaquinone in presence of 80 per cent. acetic acid. It crystallises from benzene in red, lustrous prisms and melts at 191—192°. Nitric acid converts it into a *mononitro*-derivative, which crystallises in yellowish-brown needles and melts at 232°. When the preparation of naphthophenoxazone is carried out in alcoholic solution, the *orthohydroxyanilide*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot OH$, is formed; this is insoluble in benzene, and crystallises from alcohol in red needles melting at 187—188°. *Chloronaphthophenoxazone*, prepared from chlorohydroxynaphthaquinone, crystallises in yellowish-red needles melting at 194—195°.

Naphthophenoxazime, $NH{:}C_{10}H_5<^{N}_{O}>C_6H_4$, is obtained by the condensation of orthamidophenol with hydroxynaphthaquinonimide. It crystallises from nitrobenzene in reddish-brown plates with a metallic lustre, and melts at 242—243°. When boiled with acetic acid, it is converted into naphthophenoxazone.

Benzoylorthophenylenediamine readily reacts with the naphthaquinones to form substances which are most probably anilides.

The *naphthaquinone benzoylamido-anilide*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot NHBz$, crystallises in lustrous, yellowish-red needles and melts at 238—239°. In alcoholic soda, it forms a violet solution which becomes blood-red when boiled, and then contains the sodium compound of α-naphtho-

eurhodole, formed by the removal of the benzoyl-group, followed by condensation. The corresponding *anilide* from chlorodihydroxynaphthaquinone crystallises in lustrous tablets melting at 237°, and resembles the compound just described in its properties.

Naphthoresorufin is obtained by dissolving the hydrochloride of 1 : 2 : 4-amidodihydroxynaphthalene (compare this vol., i, 237) in water, along with an excess of sodium acetate and passing air through the liquid. A pale yellow precipitate is first produced which soon becomes dark coloured. The free base, isolated from the acetyl derivative, crystallises in dark red needles with a greenish lustre, and forms carmine coloured solutions with a fiery red fluorescence. Acids readily convert it into salts, and on heating with sulphuric acid, a *sulphonic acid* is produced, the alkali salts of which are blue and readily soluble in water, their solutions having an intense red fluorescence. The *acetyl* derivative crystallises from toluene in alizarin-red needles. It is probable that in the preparation of naphthoresorufin, the pale yellow precipitate which is first formed consists of an isomeric hydroxynaphthaquinonimide and that this then reacts with a molecule of the unoxidised base to form dinaphthoresorufin, which is therefore hydroxydinapthoxazone,

$$C_{10}H_5O\lessgtr\begin{matrix}N\\O\end{matrix}\gtrless C_{10}H_5(OH).$$

A. H.

Derivatives of Hydrazine having a Closed-chain Structure. By Theodor Curtius (*J. pr. Chem.*, 1894, [2], **50**, 508—530; compare Abstr., 1893, i, 299).—The orientation of the pyrazolone derivatives dealt with in this paper is expressed by the enumeration,

$$CO\begin{matrix}<\\5\end{matrix}\begin{matrix}\overset{1}{NH}\cdot\overset{2}{N}\\CH_2\cdot\underset{\|}{CH}\\4\quad\quad 3\end{matrix}$$

3-Methylpyrazolone has been already described (Abstr., 1889, 393); it forms salts with both acids and bases, but these are of little stability.

1 : 3-*Acetylmethylpyrazolone*, $C_4N_2H_5AcO$, is the sole product of the action of acetic anhydride on 3-methylpyrazolone; it crystallises in colourless needles, melts at 140°, and is insoluble in ether and benzene but slightly soluble in alcohol and water; it behaves as a feeble acid, giving a colourless silver salt.

4 : 3-*Isonitrosomethylpyrazolone*, $OH\cdot N:C_4N_2H_4O$, obtained by the action of nitrous acid on 3-methylpyrazolone, crystallises in yellow needles, melts at 194°, and dissolves somewhat easily in cold water and in alcohol. It behaves as a powerful acid and yields a *silver salt*; this crystallises in dark red needles, and reacts with ethylic iodide at 115—120° forming the corresponding *ethylic* salt, which crystallises in yellow needles.

4 : 3-*Benzylidenemethylpyrazolone*, $CHPh:C_4N_2H_4O$, is prepared by heating a mixture of the pyrazolone with benzaldehyde in molecular proportion, and crystallising the product from alcohol; it is a brick-red, crystalline powder, melts at 204° and is insoluble in water.

3-Phenylpyrazolone, $C_3N_2H_3PhO$, is prepared by warming a mixture of hydrazine hydrate (13 grams) and ethylic benzoylacetate (50 grams) in alcohol (150 grams), and subsequently cooling. It crystallises in thick, colourless prisms, melts and decomposes at 236°, and is nearly insoluble in cold alcohol, ether or benzene. It gives sparingly soluble precipitates in solutions of salts of the heavy metals. The *hydrochloride*, $C_9N_2H_8O,HCl$, crystallises in silky needles and melts and decomposes at 195°; it dissociates when exposed to the air. 1:3-*Acetylphenylpyrazolone*, $C_9N_2H_7AcO$, crystallises in thick, colourless prisms, melts at 121°, and is sparingly soluble. 4:3-*Isonitrosophenylpyrazolone* crystallises in long, yellow needles, and gives a yellow, insoluble, silver salt.

Ethylic 3:4-*methylpyrazoloneacetate*, $C_3N_2H_2MeO{\cdot}CH_2{\cdot}COOEt$, is prepared by adding hydrazine hydrate (3·5 grams) to ethylic acetosuccinate (15 grams), diluted with an equal quantity of absolute alcohol, and warming. It crystallises in silvery laminæ, and large, colourless tables, melts at 166°, and dissolves in hot water and hot alcohol, but only sparingly in benzene or ether.

4-*Bis*-3-*methylpyrazolone*, $NH<\begin{matrix}N=CMe & MeC=N\\ CO{\cdot}CH & HC{\cdot}CO\end{matrix}>NH$, is the product obtained when ethylic diacetosuccinate (1 mol.) reacts with hydrazine hydrate (2 mols.) in alcohol; it crystallises in minute, snow-white tablets, decomposes at 250°, and is sparingly soluble; dilute acids decompose it, hydrazine being separated, but it is very stable in the presence of alkalis; it reduces ammoniacal silver solution, but not Fehling's solution; aqueous ferric chloride colours it violet.

When ethylic diacetosuccinate and hydrazine hydrate, in molecular proportion, are heated together in alcohol, a *compound* which crystallises in colourless needles and melts at 68—69° is obtained. This can be distilled unchanged at 35 mm. pressure; it is insoluble in water, but dissolves easily in hot alcohol; dilute sulphuric acid separates hydrazine from it. Fehling's solution is not altered by it; silver nitrate gives a dirty yellow precipitate. The formula and constitution of the compound are only matter of conjecture at present.

Levulinic hydrazide, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, is prepared by gently warming ethylic levulinate, diluted with an equal volume of alcohol, with hydrazine hydrate, in molecular proportion; on cooling, the new compound separates in the form of lustrous, colourless laminæ. It crystallises from water in large, colourless prisms, melts at 82° and dissolves in cold water and alcohol. The aqueous solution is neutral, gives no precipitate with benzaldehyde, and does not reduce mercuric oxide or Fehling's solution. It dissolves in both acids and alkalis, yielding hydrazine when warmed with the former. The hydrazide very readily loses a molecule of water, becoming the *anhydride*, 3-*methylpyridazinone**, $CMe<\begin{matrix}{}^{3}\\ \\ {}^{4}\end{matrix}\!\!\begin{matrix}{}^{2}N-NH^{1}\\ CH_2{\cdot}CH_2\end{matrix}\!\!>{}^{6}CO$, which crystallises from

* Previously called 3-methylpyridazolone (*Ber.*, 1893, **26**, 408).

benzene in nacreous laminæ, melts at 94°, and can be distilled at the ordinary pressure; it yields an isonitroso-derivative with nitrous acid, and is decomposed by hot dilute sulphuric acid, with separation of hydrazine.

Ethylic 3-*phenylpyridazinone*-5-*carboxylate*, $C_4N_2H_4PhO{\cdot}COOEt$, is formed when ethylic β-benzoylisosuccinate and hydrazine hydrate in molecular proportion are mixed in well cooled alcohol; it crystallises in long, silky, colourless needles, melts at 156°, and dissolves in alcohol and hot water. It yields hydrazine when heated with dilute sulphuric acid, but it does not reduce Fehling's solution. The corresponding *acid* is a colourless, crystalline powder, which melts at 116—117°, dissolves freely in hot water, and has a strong acid reaction. The *hydrazide* of the acid is obtained by heating the ethylic salt with hydrazine hydrate; it crystallises in long, colourless prisms, decomposes at 190°, and dissolves in hot water and alcohol; it reduces Fehling's solution, yields hydrazine hydrate when treated with alkalis, and gives a condensation product with benzaldehyde.

3-*Phenylpyridazinone*, $C_4N_2H_5PhO$, from methylic β-benzoylpropionate and hydrazine hydrate, crystallises in colourless prisms and needles, melts at 149—150°, and is sparingly soluble in cold solvents. It is neutral and is decomposed with difficulty by hot dilute sulphuric acid, yielding hydrazine; it does not reduce Fehling's solution.

A. G. B.

Pyrazoline and its Derivatives. By Theodor Curtius and F. Wirsing (*J. pr. Chem.*, 1894, [2], **50**, 531—554; compare Abstr., 1893, 299).—*Pyrazoline*, $NH\overset{1}{<}\overset{5}{CH_2}{\cdot}\overset{4}{CH_2}\underset{2}{N}=\underset{3}{CH}$, is best prepared by dissolving acraldehyde in three times its weight of ether, cooling, and dropping in rather more than the calculated quantity of hydrazine hydrate. The lower aqueous layer is saturated with hydrochloric acid, and evaporated at 70° until the bulk of the hydrazine has separated as dichloride; on further evaporation over caustic potash, the pyrazoline hydrochloride crystallises. This is purified by washing with strong alcohol, crystallisation from water, and precipitation from absolute alcohol by ether. The yield is about 50 per cent. The hydrazine is also conveniently removed by shaking with benzaldehyde in an acid solution, whereby benzalazine is precipitated; the excess of benzaldehyde may be removed by ether. The hydrochloride is finally distilled with caustic potash.

Pyrazoline is a colourless liquid of characteristic, amine-like odour, recalling that of cacao. It boils at 144°, and is volatile with steam and with ether vapour. It mixes in all proportions with water and alcohol, but is somewhat less soluble in ether. It forms a cloud with hydrogen chloride, and becomes yellow in the air, at the same time evolving gas, but no pyrazole is formed. It gives a white silver salt; it does not reduce Fehling's solution.

The *hydrochloride*, $C_3H_6N_2,HCl$, crystallises in large, colourless prisms, melts at 130°, and dissolves easily in water but sparingly in cold alcohol, and hardly at all in ether. Its solutions, even when very

dilute, colour woody-fibre intensely yellow. The *sulphate*, *platinochloride*, and *picrate* (m. p. 130°) are described.

Pyrazoline shows great resistance to the action of mineral acids, a fact which favours the view that it is a closed chain compound, and forbids the assumption that it is identical with acraldehydehydrazine. When boiled with concentrated aqueous alkalis, about 10 per cent. of its nitrogen is evolved as ammonia. Most oxidising agents oxidise pyrazoline drastically, causing an evolution of nitrogen, but by the action of bromine on the base or its hydrochloride, suspended in chloroform, pyrazole is produced; on the other hand, bromopyrazole is the product of the action of bromine on an aqueous solution of the hydrochloride. The connection between pyrazoline and pyrazole is thus established.

Benzaldehyde combines energetically with pyrazoline, water being eliminated. *Azobenzenepyrazoline*, $PhN{:}N{\cdot}C_3N_2H_5$, formed by the interaction of diazobenzene chloride and pyrazoline hydrochloride, crystallises in large, flat, brick-red prisms, and melts at 80°.

3-*Methyl*-5-*dimethylpyrazoline*, $C_3Me_2N_2H_3$, is obtained when mesityl oxide and hydrazine hydrate, in molecular proportion, are mixed, the product extracted with ether, and the ethereal solution distilled under diminished pressure. It is a colourless oil of basic properties and characteristic odour, and is decomposed by air; it is freely soluble in water, alcohol, and ether; with silver nitrate, its solutions yield a white precipitate which dissolves on warming. The *hydrochloride*, $C_6H_{12}N_2,HCl$, crystallises in colourless prisms, and melts and decomposes at 170°. The *picrate* (m. p. 138°), the *mercuric chloride compound*, $C_6H_{12}N_2,2HgCl_2$, the *platinochloride* (m. p. 186°), and the *methiodide* (m. p. 154°), are also described.

1 : 3-*Benzoylmethyl*-5 *dimethylpyrazoline*, $C_6N_2H_{11}Bz$, from benzoic chloride and the pyrazoline, crystallises in colourless, felted needles, and melts at 236°.

A *compound*, $C_{24}H_{34}N_6O_{12}$, forming colourless crystals, melting at 223°, and freely soluble in water, was obtained as a bye-product in the preparation of 1-phenylpyrazoline.

Benzylidene-1-*phenylpyrazoline*, $CHPh{:}C_3N_2H_3Ph$, the condensation product of benzaldehyde with 1-phenylpyrazoline, is a white powder, and melts at 235°. A second modification was obtained in the form of an ochre-yellow powder of ill-defined melting point.

Isonitroso-1-*phenylpyrazoline*, $C_3N_2H_3Ph{:}NOH$, crystallises in small, brick-red needles, and melts at 148°. *Benzeneazo*-1-*phenylpyrazoline*, $C_3N_2H_4Ph{\cdot}N_2Ph$, crystallises in brilliant, purple-red needles, melting at 156°; its *hydrochloride* is described.

When hydrogen chloride is passed into an ethereal solution of 1-phenylpyrazoline, *bisphenylpyrazoline hydrochloride*, $C_{18}H_{20}N_4,HCl(?)$, separates as a greenish oil, which crystallises in slender, colourless needles. It rapidly loses hydrogen chloride, even in air; its acid solutions in alcohol and benzene are dark green by reflected light, but purple-red by transmitted light; it melts at 175°. The corresponding *base* crystallises in yellow needles, melts at 221°, and dissolves freely in hot benzene, but only sparingly in ether, and not in water. The ethereal solution has a blue fluorescence. The base

dissolves in glacial acetic acid forming a cherry-red solution, whilst with strong sulphuric acid it yields a cherry-red or blue solution, and with strong nitric acid an indigo-blue solution.

A *compound* of the formula $C_9H_{17}N_2I$ is obtained from allylic iodide and hydrazine hydrate; it forms colourless crystals, and melts at 102°.

A. G. B.

Action of Ethylic Diazoacetate on Unsaturated Ethylic Salts. By EDUARD BUCHNER and AUGUST PAPENDIECK (*Ber.*, 1895, **28**, 221—224).—Ethylic diazoacetate and benzylideneacetoacetate, when boiled together for three or four days at 50—75°, condense to form *ethylic phenylacetylpyrazolinedicarboxylate*, probably

$$NH<\begin{matrix}N=\!=\!=C\cdot COOEt\\ CHPh\cdot CAc\cdot COOEt\end{matrix};$$

this crystallises in colourless needles and melts at 76°; its *phenylhydrazone* crystallises from alcohol in needles melting at 135—136°, from ether in plates melting at 110—111°. On hydrolysis of the ethylic salt, the free *acid* with $2H_2O$ is obtained; this forms a *diphenylhydrazide* and a *calcium salt* with $5H_2O$; its silver salt, when heated in a current of carbonic anhydride, yields 5-phenylpyrazole (Abstr., 1893, i, 282; this vol., i, 192). When the ethylic salt is distilled under 25 mm. pressure, an oil passes over at 230—242°; this solidifies to colourless plates melting at 101°; it does not contain nitrogen.

C. F. B.

Phenometadiazine Derivatives. By AUGUST BISCHLER and MARTIN LANG (*Ber.*, 1895, **28**, 279—293; compare Abstr., 1893, i, 609).—Pheno-β-methylmetadiazine has been previously described (Abstr., 1891, 745). It is not affected by dilute permanganate, but chromic acid in acetic acid solution converts it into *pheno-β-methylhydroxymetadiazine*, $C_6H_4<\begin{matrix}N=\!=\!=CMe\\ C(OH):N\end{matrix}$, which crystallises in white, silky needles, and melts at 231·5—232°. It appears to be identical with the substance described by Weddige (Abstr., 1887, 1043) as anhydroacetylorthamidobenzamide. The *platinochloride* decomposes above 300°, and the *dichromate* deflagrates at 175—176°. Propionic anhydride converts orthamidobenzaldehyde into an oil which, on treatment with alcoholic ammonia, yields *pheno-β-ethylmetadiazine;* this is a yellow, oily liquid, which has a sp. gr. of 1·0899 at 20°, and boils at 247—249° (722 mm.). The *hydrochloride*, $C_{10}H_{10}N_2,HCl + H_2O$, is obtained by passing hydrogen chloride into an ethereal solution of the metadiazine. *Pheno-β-ethyl-α-hydroxymetadiazine* may be sublimed in snow-white, woolly needles, melting at 227—228°. *Pheno-β-normalpropylmetadiazine* boils at 257—259°, and also forms a *hydrochloride* and a *platinochloride*. Its *hydroxy-compound* crystallises in white, bulky needles, which melt at 205°. The *platinochloride* crystallises well. *Pheno-β-isopropylmetadiazine* boils at 253—255°, whilst the corresponding *hydroxy-derivative* crystallises in concentric groups of white needles, melting at 195—196°.

Benzoylamidobenzaldehyde, $NHBz\cdot C_6H_4\cdot CHO$, forms stellate groups

of yellowish-white, slender needles, melting at 73—74°. Pheno-β-phenylmetadiazine has been previously described by Gabriel and Jansen (Abstr., 1890, 1442). The *hydrochloride* crystallises in needles, and is decomposed by warm water. The *platinochloride* and *picrate* are crystalline. *Pheno-β-phenylhydroxymetadiazine* forms lustrous, white needles, and melts at 235—236°. *Pheno-β-benzylmetadiazine* is an odourless, yellow, crystalline mass, which melts at 59—60°, but could not be obtained quite pure. The *hydroxy-compound* forms slender, matted needles, melting at 177°.

Formylamidobenzaldehyde could not be obtained either directly or indirectly. In order to prepare phenometadiazine itself, *ethoxalyl-orthamidobenzaldehyde*, $COOEt\cdot CO\cdot NH\cdot C_6H_4\cdot CHO$, was prepared by the action of ethoxalyl chloride on the aldehyde. This crystallises in long, silky needles, melting at 196°, and on hydrolysis yields the corresponding *oxamic acid*, which crystallises in stellate groups of needles, and melts and decomposes at about 163—164°. As the formyl-compound could not be obtained from it, the acid was treated directly with alcoholic ammonia; in this way, a small amount of a yellow oil was obtained, which had the characteristic smell of the phenometadiazines, resembling that of mice, and had the composition of phenometadiazine. The amount obtained was too small for any further experiments.

When crude phenylacetylorthamidobenzaldehyde is treated with alcoholic potash, it yields a substance which crystallises in white needles and melts at 234—235°. This compound, which is probably *phenylhydroxyquinoline*, is being further investigated. A. H.

Semicarbazide. By Johannes Thiele and Otto Stange (*Annalen*, 1894, **283**, 1—46; compare Abstr., 1891, 452, and 1894. i, 165).—*Orthonitrobenzylidenesemicarbazide*, $NH_2\cdot CO\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2$, is obtained by adding orthonitrobenzaldehyde dissolved in alcohol to an aqueous solution of semicarbazide hydrochloride. It crystallises in lemon-yellow needles, which melt and decompose at 256°; the solution in hot soda is red. *Metanitrobenzylidenesemicarbazide* forms pale yellow needles, which melt at 246°, and dissolve in hot soda with development of a yellowish-brown coloration. *Paranitrobenzylidene-semicarbazide* separates from hot alcohol in yellowish-white crystals, melting at 221°; it crystallises from water in lemon-yellow needles containing $2H_2O$. The *sodium* salt is brownish-red.

1 : 2-*Diphenylhydroxytriazine*, $N\lessdot\begin{matrix}C(OH){:}N\\CPh\cdot CPh\end{matrix}\gtrdot N$, is obtained by boiling a solution of semicarbazide hydrochloride, which has been neutralised with magnesium carbonate, with an alcoholic solution of benzile (1 mol.) for 15 hours; it crystallises in pale yellow needles, and melts at 218°. The *ethyl ether* forms colourless needles, melting at 105°.

Ethylic acetoacetate-semicarbazide, $NH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot COOEt$, is prepared by agitating the solution of semicarbazide hydrochloride with ethylic acetoacetate in presence of sodium acetate; it melts at 129°. When warmed with ammoniacal silver solution, the substance is oxidised, and evolution of gas takes place; potassium permanga-

nate is decolorised on heating. Hydrogen cyanide does not give rise to an additive compound. When heated at 120°, ethylic acetoacetate-semicarbazide is converted into 3-methylpyrazolone, which is also formed on boiling the aqueous solution.

3-Methylpyrazolone-1-carbonamide, $\begin{matrix}N=\!\!=\!\!=\!\!=CMe\\ |\\ N(CONH_2)\cdot CO\end{matrix}>CH_2$, is produced when the foregoing compound remains in contact with ammonia for two days; the residue obtained on evaporating the liquid in a vacuum, is dissolved in cold methylic alcohol, and precipitated with ether. The substance melts at 192°, and is converted into methylpyrazolone when the aqueous solution is warmed. Ferric chloride develops a blue coloration, which becomes brown when heated.

Ethylic 3-methylpyrazolone-1-carbonyl-β-amidocrotonate,

$$COOEt\cdot CH{:}CMe\cdot NH\cdot CO\cdot \begin{matrix}N{:}CMe\\ |\\ N\!-\!CO\end{matrix}>CH_2,$$

is obtained by agitating semicarbazide hydrochloride with excess of ethylic acetoacetate in presence of soda; it forms small prisms, which melt and decompose at 176°. Ferric chloride produces an intense blue coloration. The *sodium* salt is colourless. When distilled in a current of steam, the substance is decomposed into ethylic acetoacetate, ammonia, carbonic anhydride, and methylpyrazolone.

Carbonamidohydrazoisobutyronitrile, $NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CN$, is obtained by the action of hydrogen cyanide on acetone-semicarbazide, and crystallises in prisms, which melt at 144°. It has powerful reducing properties, and is decomposed into hydrogen cyanide and acetone-semicarbazide when the aqueous solution is heated on the water bath.

Carbonamidoazoisobutyronitrile, $NH_2\cdot CO\cdot N{:}N\cdot CMe_2\cdot CN$, is obtained by oxidising the hydrazo-compound with potassium permanganate in presence of sulphuric acid; it forms lemon-yellow plates, which melt at 78°. It is decomposed by cold, dilute alkalis, with liberation of nitrogen, carbonic anhydride, ammonia, and isopropylic cyanide.

Carbonamidohydrazoisobutyramide, $NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CONH_2$, is formed by the action of fuming hydrochloric acid on the nitrile; it melts and decomposes at 205—206°. When oxidised with potassium permanganate, it yields *carbonamidoazoisobutyramide*, which separates from hot water in deep yellow crystals, and melts and decomposes at 151°.

Carbaminazoimide, $NH_2\cdot CO\cdot N_3$, is obtained by adding sodium nitrite (1 mol.) to the aqueous solution of semicarbazide hydrochloride; it crystallises in large prisms, which melt at 92—93°. The aqueous solution is acid, and yields azoimide when boiled. Mercuric chloride produces a white precipitate. The dry solid is volatile, and explodes when heated. One half the total quantity of nitrogen is liberated by a cold solution of stannous chloride in hydrochloric acid. The colourless, highly explosive, *silver* salt is insoluble in water; it dissolves in ammonia and in dilute nitric acid, whilst concentrated acid decomposes it into silver azoimide, carbonic anhydride, and

ammonia. Carbaminazoimide is also formed by the action of nitrous acid on hydrazodicarbonamide.

Hydrazodicarbonimide (*urazole*), $\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CO\end{matrix}>NH$, is obtained by heating hydrazocarbonamide at 200° for five hours; it melts at 244°. The aqueous solution has powerful reducing properties, and yields a white precipitate with mercuric chloride; cupric acetate produces a green precipitate. Oxidising agents develop a red coloration, due to the formation of azodicarbonimide, which, however, has not been isolated, owing to its extreme volatility and unstable character. The *silver* salt is colourless, and is not decomposed by light; the *sodium* salt separates from water in small plates, which contain $2H_2O$. The *phenyl* derivative, *hydrazodicarbonanil*, is obtained by heating a mixture of hydrazodicarbonamide and aniline hydrochloride (1 mol.) at 220° for four hours, diphenylcarbamide being formed at the same time. It crystallises from water in prisms, and melts at 203°. The *silver* salt is pale yellow. Oxidising agents convert it into the *azo*-derivative, $\begin{matrix}N\cdot CO\\ ||\\ N\cdot CO\end{matrix}>NPh$, a dark red solid, having a pungent odour.

M. O. F.

r-**Coniïne.** By Albert Ladenburg (*Ber.*, 1895, **28**, 163—165).—When 4 grams of *l*-coniïne are mixed with 2 grams of *d*-coniïne at the ordinary temperature, no change of specific gravity occurs, but there is a fall of temperature. This last must be due to the formation of an endothermic compound, and *r*-coniïne is thus a compound, and not a mere mixture, of the two optically active varieties, in spite of the fact that it has the same specific gravity as these. It is consequently not necessary, as E. Fischer thinks it to be, that a racemic compound should have physical properties different from those of its active components.

d- and *r*-coniïne have respectively 1·4548 and 1·4581 as their indices of refraction for the D line at 15°, and they dissolve to the extent of 1·80 and 1·93 parts in 100 of water. C. F. B.

Conium Alkaloïds. By Richard Wolffenstein (*Ber.*, 1895, **28**, 302—305; compare Abstr., 1894, i, 627).—The author has detected coniceïne in a specimen of coniïne, prepared from *Conium maculatum*. This is identical with the γ-coniceïne described by Hofmann (Abstr., 1885, 562). The *hydrochloride* melts at 143°, the *hydrobromide* at 139°, and the *hydriodide* at 102°. The *stannochloride* crystallises in plates, melting at about 215°; the *picrate* melts at 62°, and the *aurochloride* at 69—70°. Coniceïne is about 17 times as poisonous as coniïne, and it is probable that the uncertain effect of coniïne when administered may be due to an unsuspected presence of coniceïne.

Coniceïne is optically inactive, and is not resolved into active components by fractional crystallisation with dextrotartaric acid. It follows from this that the ethylene bond must be between the asymmetric carbon atom of coniïne and a neighbouring atom, so that its constitutional formula will be $NH<\begin{matrix}CH_2\cdot CH_2\\ CPr:CH-\end{matrix}>CH_2$. A. H.

Cinchotenine. By ZDENKO H. SKRAUP (*Ber.*, 1895, **28**, 12—16).—A preliminary notice; the full paper is to appear in the *Monatshefte*. Quinine, quinidine, cinchonine, and cinchonidine are known to yield "tenines" and formic acid when cautiously oxidised with permanganate; cinchonine, $C_{19}H_{22}N_2O$, for example, yields cinchotenine, $C_{18}H_{20}N_2O_3$. It is also known that they are di-tertiary bases, and that they contain a hydroxyl group. This is now shown to be true of the "tenines" also, in particular of cinchotenine, the ethylic salt of which (see below) forms a compound with two molecules of ethylic iodide; this is not decomposed by alkali carbonates. It yields a benzoyl derivative. Further, the "tenines" contain a carboxyl group, for they, as well as their benzoyl derivatives, form metallic salts; they also yield ethylic salts, and acid chlorides. They do not form additive compounds with hydrogen iodide, whereas the alkaloïds from which they are derived, do so; it is thus probable that these alkaloïds contain an unsaturated (vinyl) group, $\cdot CH{:}CH_2$, as a side chain, and that this group is converted into carboxyl and formic acid when the alkaloïds are oxidised to "tenines." Moreover, the bases that occur in the commercial alkaloïds, and contain in the molecule 2 atoms of hydrogen more than these (cinchotine, &c.), probably have an ethyl group in place of this vinyl group. Finally, it is pointed out that the relation of cincholeupone, $C_9H_{17}NO_2$ (formed by oxidation of cinchotine), meroquinine, $C_9H_{15}NO_2$ (by oxidation of cinchonine), and cincholeuponic acid, $C_8H_{13}NO_4$, is that of dihydroalkaloïd to alkaloïd to "tenine;" for example, of cinchotine : cinchonine : cinchotenine. C. F. B.

History of Aconitine. By MARTIN FREUND (*Ber.*, 1895, **28**, 192—195).—Controversial note in reply to Dunstan's claim to priority (Abstr., 1894, i, 308).

Cytisine and Ulexine. By PIETER C. PLUGGE (*Arch. Pharm.*, 1894, **232**, 557—558) and by ALFRED PARTHEIL (*ibid.*, 558—559; compare Partheil, Abstr., 1893, i, 119, and 1894, i, 558).—A question of priority.

Pseudopelletierine. By CHARLES TANRET (*Bull. Soc. Chim.*, 1894, [3], **11**, 422—423).—A protest against the substitution, by Ciamician and Silber (Abstr., 1894, i, 154), of the name granatonine for that of pseudopelletierine. JN. W.

Chondroitin-sulphuric acid. By CARL T. MÖRNER (*Zeit. physiol. Chem.*, 1895, **20**, 357—364).—This substance, originally named chondroitic acid, is an ethereal hydrogen sulphate, and has been found in certain forms of cartilage. The present research shows that all kinds of cartilage, from 20 different situations in the body, and also cartilaginous tumours or enchondromata yield it. It is, moreover, a substance characteristic of cartilage, and is not yielded by any other tissue of the body, 14 of which were investigated. W. D. H.

Coagulation of Proteïds by Mechanical Means. By W. RAMSDEN (*Archiv. für Anat. u. Physiol.; physiol. Abth.*, 1894, 517—

534).—By mechanical means, such as shaking with sand, or even pouring from one test-tube to another, a solution of egg-white deposits insoluble proteïd, reminding one of fibrin filaments, which also it resembles in its difficulty of solubility. By prolonged shaking, 96 per cent. of the proteïd present was separated. Other proteïds behave similarly, but, as a rule, in a less degree, namely, egg globulin, vitellin, the proteïds of blood-plasma, myosinogen, potato proteïd, plant vitellin, alkali albumin, and some specimens of caseïnogen.

W. D. H.

Crystallisation of Serum Albumin. By AUGUST GÜRBER (*Sitzungsb. Würzburger Phys. med. Ges.*, 1894).—Crystals of serum-albumin may be obtained in the course of some weeks from the serum of horse's blood by Hofmeister's method. A new method, not yet divulged, has enabled the author to obtain them more rapidly; the crystals indicate that there are three albumins in the serum. They could not be obtained from ox serum. W. D. H.

The Combination of Sulphur in Albumin. By EUGEN BAUMANN (*Virchow's Archiv*, 1894, **138**, 560—562).—**Answer to the foregoing.** By ERNST SALKOWSKI (*ibid.*, 562—564). Polemical.

Sulphur in various Keratin Substances. By P. MOHR (*Zeit. physiol. Chem.*, 1895, **20**, 403—406).—Different authors give different percentages of sulphur in different keratins. In the present research, keratin was prepared from various sources, and, as the following table shows, the variations in the percentage of sulphur are considerable.

Source of keratin.	Sulphur per cent.	Source of keratin.	Sulphur per cent.
Woman's hair—dark blonde ..	4·95	Sheep's wool.....	3·68
Girl's hair—dark brown.....	5·34	Goose feathers	2·59—3·16
Boy's hair—red blonde.....	4·98	Pig's hoof	2·69
Boy's hair—red.....	5·32	Calf's hoof	3·57
Rabbit's hair	4·01	Ox hoof, white	3·49
Calf's hair	4·35	Ox hoof, black	3·45
Horsehair	3·56		
Pig's hair.....	3·59		

W. D. H.

Amyloïd. By ARMIN TSCHERMAK (*Zeit. physiol. Chem.*, 1895, **20**, 343—356).—The substance called amyloïd by Virchow, which occurs in a certain form of pathological degeneration, has been shown by Kekule, Kühne, and others to be proteïd in nature.

The present research confirms this, and, moreover, shows that the material in question dissolves easily in alkalis, and less easily in organic and mineral acids, and on peptic and tryptic digestion, and on heating it in a sealed tube in water. The result of the solution is,

first, unchanged amyloïd, then albuminate, and, on more prolonged digestion, primary and secondary albumoses and peptone. These products of digestion give the same colour reactions as the original material, sometimes even more intensely.

Amyloïd is regarded, like hyalin, as a modified coagulation product of the circulating proteïd, probably serum albumin, not fibrin.

W. D. H.

Methæmoglobin. By J. A. Menzies (*J. Physiol.*, 1895, **17**, 402—414).—Oxyhæmoglobin becomes converted into methæmoglobin as the result of exposure to the air, either in solution or in the dried condition; and also as the result of the action of many reagents, of which the following were investigated in the present research: glycerol, potassium chlorate, permanganate and ferricyanide, iodine, amylic nitrite, potassium nitrite, sodium fluoride, and certain acids.

When it is produced by decomposition, the solution becomes acid, and if decomposition proceeds further, whereby the reaction changes to alkaline, a reconversion of hæmoglobin takes place. If produced by the action of reagents, the further action of the same reagents gives rise to hæmatin, which is precipitated, unless held in solution by acids. In the case of potassium ferricyanide, the hæmatin passes into the condition of cyanhæmatin.

Methæmoglobin cannot be distinguished from hæmatin by its spectrum alone, but only by the change produced by a reducing agent; it yields hæmoglobin on reduction, whilst hæmatin yields hæmochromogen; but in the case of potassium chlorate or ferricyanide or of iodine, the hæmochromogen is after a time gradually transformed into hæmoglobin. The action of the nitrite is considered to be due to the liberation of nitrous acid, and it is suggested that the liberation of acid substances from the other reagents employed is the cause of their action.

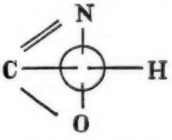
In the spectrum of methæmoglobin, the only constant feature is the band in the red, but even this varies in position; bands 2 and 3 become paler till they disappear, as the formation of methæmoglobin becomes completed. Band 4 becomes swamped in the general absorption of the violet end as the formation of hæmatin occurs. Methæmoglobin is regarded as an intermediate product between oxyhæmoglobin and hæmatin.

W. D. H.

Action of Acids on Hæmoglobin. By J. A. Menzies (*J. Physiol.*, 1895, **17**, 415—422).—Acetic, oxalic, phosphoric, hydrochloric, nitric, and sulphuric acids act on hæmoglobin, converting it first into methæmoglobin, then into hæmatin. The position of the typical absorption band in the red varies with the different acids. By using dilute mineral acid of a certain strength, oxyhæmoglobin can be resolved into a proteid, which remains in solution, and hæmatin, which is precipitated. The latter, when dissolved in dilute acid or alkali, yields hæmochromogen, which, on being mixed with some of the colourless proteid solution, becomes converted into hæmoglobin.

W. D. H.

Organic Chemistry.

Tautomerism. By Adolph Claus (*J. pr. Chem.*, 1895, [2], **51**, 338—343).—The author suggests that in tautomeric substances, which yield isomeric series of derivatives, but do not themselves exist in more than one form, one of the atoms (usually a hydrogen atom but sometimes possibly one of sodium, &c.) is not combined with any one particular atom of the molecule, but is held in combination by a common "central" linking with several of the other atoms of the molecule. Cyanic acid, for example, would therefore be represented by the formula 

A. H.

Cyanoethers. By Albert Colson (*Compt. rend.*, 1894, **119**, 1213—1215).—The action of cyanogen chloride at the ordinary temperature on a solution of paraxylene in moist ether, yields ammonium chloride, a large quantity of carbonic anhydride, and a solid substance which melts at 48° and seems to be a derivative of ether rather than of paraxylene. The action of cyanogen chloride on washed ether in presence of sunlight yields ammonium chloride, carbonic anhydride, and urethane. The latter is a constant product of the action of cyanogen chloride on ether, as Gautier has observed.

The prolonged action of light on the mixture of cyanogen chloride and ether results in the formation of the compound CN·CHMe·OEt, which has the composition of ethyllactonitrile. It has an ethereal odour and a burning alcoholic taste, is miscible with water, alcohol, and ether, and boils at 129—130°; sp. gr. = 0·87 at 12°. Longer exposure of the original mixture to light yields a compound of the same composition, which, however, is very slightly soluble in water. It boils at 131° under a pressure of 765 mm., and its molecular weight, like that of the soluble compound, is 99; sp. gr. = 0·824 at 12°. It has an ethereal odour and a burning taste, and is miscible with alcohol and ether.

The soluble and insoluble compounds seem to be physical isomerides; they are both very stable, and, when fused with potash, yield ammonia without any formation of a cyanide. From their mode of formation, it would seem that they are related to lactic acid and not to hydracrylic acid. C. H. B.

A New Class of Nitriles. By Albert Colson (*Compt. rend.*, 1895, **120**, 101—104).—The author has previously described (preceding abstract) two isomeric cyanoethers of the type OR·CHMe·CN, which are very stable, and differ from the lactic nitrile OH·CHMe·CN and its homologues discovered by Gautier and Sampson, in that when fused with potassium hydroxide they lose their nitrogen as ammonia.

The author gives the name *cyanal* to this so-called lactic nitrile and its homologues.

With acetic chloride, cyanal yields the acetate AcO·CHMe·CN, which boils at 169° (uncorr.) under a pressure of 760 mm.; sp. gr. = 1·052 at 0°, and 1·032 at 14°; vapour density normal. It dissolves in 25 times its weight of water, and the solution yields no precipitate with silver nitrate, even after a long time; it is also soluble in ether, alcohol, acetic acid, &c. Cyanal acetate has none of the characteristic properties of nitriles or secondary alcohols. It hydrolyses very slowly even at 140°, but eventually yields aldehyde, acetic acid, and hydrocyanic acid in equal molecular proportions. If cyanal acetate is added to an ammoniacal solution of silver nitrate mixed with some potassium hydroxide, there is immediate formation of a silver mirror. With dry hydrogen chloride, it yields a crystalline compound which will be described later.

Cyanal propionate, $C_3H_5O_2$·CHMe·CN, obtained in a similar way, has similar properties. It boils at 181—182° under a pressure of 760 mm.; sp. gr. = 1·022 at 0°, and 1·004 at 18°. It has a sweet taste, and dissolves in 30 times its weight of water.

Propylcyanal acetate, AcO·CHEt·CN, boils at 183° under a pressure of 762 mm.; sp. gr. = 1·019 at 0°, and 1·006 at 12·5°. It is only very slightly soluble in water, and splits up into its proximate constituents under the influence of alkalis. C. H. B.

Brown-coal Tar. By Friedrich Heusler (*Ber.*, 1895, **28**, 483—498; compare Abstr., 1892, 1075).—The fraction of brown-coal tar boiling below 180° contains:—1. Paraffins, in quantity increasing with rise of boiling point. 2. Naphthenes, in small amount. 3. Aromatic hydrocarbons, in quantity decreasing with rise of boiling point. 4. Hydrocarbons of the ethylene series (hexylene, heptylene). 5. Thiophens (thiotolen, thioxen). 6. Ketones (methyl ethyl ketone); and 7. Nitriles, in very small amount.

A sample of coal-tar oil was also proved to contain acetone. C. F. B.

Formation of Normal Alkylic Sulphates when Tar Oils are Washed with Sulphuric acid. A New Method of Separating Alkylic Sulphates and Sulphonates. By Friedrich Heusler (*Ber.*, 1895, **28**, 498—501).—The oil obtained when brown-coal tar oil, boiling at 150—160°, is washed with strong sulphuric acid is proved to contain decylic sulphate (11·3 grams in 100 c.c.), for, when mixed with aniline and allowed to remain, it yields aniline decylic sulphate, $C_{10}H_{21}O·SO_2·ONH_3Ph$, together with decylene.

Aniline alkylic sulphates are decomposed by boiling with aniline into aniline sulphate and alkylene; aniline alkylsulphonates are not so decomposed. If, therefore, a mixture of sulphate and sulphonate is boiled with aniline and then distilled with steam, aniline and the alkylene from the sulphate pass over, whilst the sulphonate remains behind. C. F. B.

Salts of the Acid $H_2S_2O_2$ (Thiosulphurous acid ?). By Felix Lengfeld (*Ber.*, 1895, **28**, 449—451).—The *methylic* salt, $S_2(OMe)_2$,

is obtained by adding dry sodium ethoxide to a cold solution of sulphur monochloride in light petroleum. It is a pale yellow oil which boils at 41—42° under a pressure of 23 mm., and has an excessively disagreeable, pungent order. The *ethylic* salt is colourless; it boils at 71—72° under a pressure of 28 mm. M. O. F.

Calcium Ethoxide. By Robert de Forcrand (*Compt. rend.*, 1894, **119**, 1266—1268).—When calcium carbide, CaC_2, is heated with absolute alcohol at 180°, gas is liberated which is a mixture of acetylene with two other hydrocarbons, one of which is probably methane and the other an olefine containing a larger number of carbon atoms, the composition of the gaseous mixture corresponding with the formula C_4H_6, and the reaction being $CaC_2 + 2C_2H_6O = Ca(OEt)OH + C_4H_6$. When the solid product is dried in the air and then for a short time over sulphuric acid, it has the composition 3CaO,4EtOH, and is not calcium ethoxide, but an additive compound of calcium oxide and alcohol, analogous to that obtained by the action of barium oxide on methyl alcohol. Very prolonged drying over sulphuric acid results in loss of alcohol and formation of the compound Ca(OEt)OH. Colourless crystals form in the sealed tubes before they are opened, but change to a white, amorphous powder on drying. C. H. B.

Ether. By Lassar-Cohn (*Annalen*, 1895, **284**, 226—232).—In estimating lactic acid by agitating the ethereal extract with water and estimating the aldehyde formed when the solution is oxidised with manganese dioxide and sulphuric acid (Boas's method), it is obviously of the first importance to obtain ether uncontaminated with alcohol. The method of purification adopted by the author is as follows. 1500 c.c. of ether is heated with 25 grams of sulphuric acid, 20 grams of potassium dichromate, and 50 c.c. of water for 24 hours in a reflux apparatus; it is then distilled and mixed with phenylhydrazine, from which it is distilled in 24 hours. A few grams of salicylic acid is then dissolved in the ether, which is again distilled after 24 hours, and the whole process is repeated. On shaking the product with water, and boiling the aqueous extract with sulphuric acid and manganese dioxide for a few minutes, Nessler's reagent produces a slight precipitate, which corresponds with about 0·001 per cent. of aldehyde. M. O. F.

Action of Chlorine on Secondary Alcohols. By A. Brochet (*Compt. rend.*, 1894, **119**, 1270—1272).—The action of chlorine on secondary alcohols is much simpler than its action on primary alcohols. The hydrogen of the CHOH group is removed, with formation of a ketone, and substitution of chlorine for hydrogen takes place in the attached radicles in a manner determined by the nature of the latter.

Isopropylic alcohol, when strongly cooled and treated with dry chlorine, yields neither acetone nor isopropylic chloride. The product is *unsymmetrical tetrachloracetone*, $CH_2Cl{\cdot}CO{\cdot}CCl_3$, no lower chlorine derivative being obtained at any stage of the action. This boils at

183°; sp. gr. = 1·624 at 15°/4°; n_d = 1·497 at 18°. When treated with very dilute aqueous potash, it yields chloroform and potassium mono- and tri-chloracetates, without any methylene chloride, and hence the symmetrical derivative, $CO(CHCl_2)_2$, is not present. It would seem that alkalis can act on the unsymmetrical tetrachloracetone in two ways: (1) $CH_2Cl{\cdot}CO{\cdot}CCl_3 + KOH = CH_2Cl{\cdot}COOK + CHCl_3$ and (2) $CH_2Cl{\cdot}CO{\cdot}CCl_3 + KOH = CH_3Cl + CCl_3{\cdot}COOK$.

The action of chlorine on isopropylic alcohol is obviously not strictly analogous to the action of bromine, as observed by Friedel and by Etard.

Methylhexylcarbinol rapidly absorbs dry chlorine, but the liquid must be heated towards the close of the action. The product is a pentachloroketone, $C_8H_{11}Cl_5O$, which yields chloroform when treated with alkalis, and probably has the constitution $C_5H_{11}{\cdot}CCl_2{\cdot}CO{\cdot}CCl_3$. It is a colourless, viscous liquid, which boils at 174° under a pressure of 15 mm., but decomposes when distilled under the ordinary pressure; sp. gr. = 1·401 at 15°/4°; n_d = 1·506 at 21°. It is insoluble in water, but has a burning taste, and an extremely persistent and disagreeable odour (compare Abstr., 1894, i, 484). C. H. B.

Purification of Alcohols, Sugars, and other Organic Substances. By Edme J. Maumené (*Compt. rend.*, 1894, **119**, 1014—1016).—Alcohols can be purified by adding a small quantity of an aqueous solution of potassium permanganate and mixing as intimately as possible. If a small quantity of acid is produced, chalk may be added. The same treatment may be applied to both white and red wines, and their flavour is thereby improved, without any loss of bouquet, and without appreciable loss of colour in the case of red wines. A small quantity of manganese oxides, if any, remaining in the liquid, will be quite innocuous.

Permanganate solution may also be used for the purification of sugar, from which it removes all taste or odour of beetroot or sugar cane. It is likewise employed in Algeria to purify the drinking water used by the troops. C. H. B.

Specific Rotatory Power of Acetylmaltose and of Maltose. By Alexander Herzfeld (*Ber.*, 1895, **28**, 440—443; compare Ling and Baker, Trans., 1895, 212).—The discrepancy which appears between the author's determination of the specific rotatory power of acetylmaltose and the value obtained by the above-mentioned investigators (*loc. cit.*), must be attributed to the character of the solvent employed; the dissimilarity of crystalline form exhibited by the two preparations remains, however, unexplained.

Acetylmaltose in chloroform solution has $[\alpha]_D = +61{\cdot}01°$, in alcohol $[\alpha]_D = +60{\cdot}02°$, whilst if benzene is employed as solvent, $[\alpha]_D = +76{\cdot}54°$.

The phenylhydrazone of maltose is decomposed by benzaldehyde; similarly, mannose has been obtained from the phenylhydrazone through the agency of this substance. M. O. F.

Nitration of Aliphatic Bases. By EUGEN BAMBERGER and ALFRED KIRPAL (*Ber.*, 1895, **28**, 535—538; compare this vol., i, 273).—By heating the nitrates of the respective bases with acetic anhydride, the following nitro-derivatives were prepared. Nitropiperidine, $C_5NH_{10}\cdot NO_2$, mixed with some nitrosopiperidine,

$$C_5NH_{10}\cdot NO.$$

Nitrodimethylamine, $NMe_2\cdot NO_2$. These substances are identical with those prepared by Franchimont by an indirect method. C. F. B.

Isomeric 2 : 5-Diamidohexanes. By HEINRICH GÜNTER and JULIUS TAFEL (*Ber.*, 1895, **28**, 379—385).—Diamidohexane,

$$NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2,$$

prepared by reducing the biphenylhydrazone of acetonylacetone (Abstr., 1889, 976), can be separated into two isomerides by means of its dibenzoyl derivative, which is found to be a mixture of two substances that can be separated by the difference in their solubilities in alcohol, and then reconverted into diamidohexanes by heating with hydrochloric acid at 145°. The diamidohexanes themselves exhibit a like chemical behaviour, and doubtless stand to one another in the relation of racemic to inactive mesotartaric acid, although it has not as yet been possible to separate either of them into optically active constituents. They boil at nearly the same temperature, and as this is also the case with ethylic racemate and mesotartrate, substances of quite different constitution from the diamidohexanes, the author thinks it may be a general law that "two substances that are only isomeric in the sense of racemic and mesotartaric acids, have approximately the same boiling point." One diamidohexane and its derivatives melt at a higher temperature, and are less soluble than the corresponding isomerides; the former are denoted by ϕ, the latter by χ.

ϕ-Diamidohexane boils at 175·5° under 753 mm. pressure; the *platinochloride* decomposes at 230° without melting; the *dibenzoyl* derivative melts at 238° (uncorr.), and, when melted, or when allowed to remain in strong hydrochloric acid solution, is transformed into a modification insoluble in hydrochloric acid.

χ-Diamidohexane boils at 174·5—175° under 752 mm. pressure; the *platinochloride* melts and decomposes at 211°, and the *dibenzoyl* derivative melts at 193—198°. C. F. B.

Combination of Hexamethylenetetramine with Silver Salts. By MARCEL DELÉPINE (*Compt. rend.*, 1894, **119**, 1211—1213).—The compound $C_6H_{12}N_4,AgNO_3$ is obtained in tabular crystals by mixing aqueous solutions of its proximate constituents; the compound $C_6H_{12}N_4,4AgCl$ is formed by the action of hydrochloric acid on the preceding compound, or of hexamethylenetetramine hydrochloride on silver nitrate solution, and crystallises from ammonia in prisms. The compound $5C_6H_{12}N_4,3Ag_2CO_3 + 15H_2O$ is obtained by the action of air or carbonic anhydride on an ammoniacal solution of silver oxide and hexamethylenetetramine, and forms acicular crystals. All these compounds are unstable, and yield silver mirrors when their solutions are heated. C. H. B.

Action of Ammonia on Methylenic Chlorobromide. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1894, [3], **11**, 549—556).—Methylenic chlorobromide (1 mol.) reacts with saturated methylic alcoholic ammonia (2 mols.) at the ordinary temperature, quantitatively, but very slowly, yielding *hexamethylenetetramine hydrobromide*, $C_6H_{12}N_4,HBr$, a substance forming hard, brilliant, highly-refractive crystals, and identical with that prepared from hexamethylenetetramine made from formaldehyde. At 60—70°, the action is complete in two hours. The hydrobromide, like the free base, is converted by nitrous acid into dinitrosopentamethylenetetramine, $C_5H_{10}N_4(NO)_2$. It is extremely easily hydrolysed by water, and is converted into the free base by lime, but the yield is very poor. It forms a double salt with silver bromide, so that the base cannot be liberated by means of silver oxide. The hexamethylenetetramine dibromide precipitated by bromine from solutions of the base is not amorphous, as stated by Horton (Abstr., 1888, 1051), but, on exposure to air, loses excess of bromine, and then crystallises in characteristic, microscopic, oblique parallelopipeda. JN. W.

Action of Ammonia on Methylenic Chloride. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1894, [3], **11**, 556—557).—Methylenic chloride interacts with saturated methylic alcoholic ammonia scarcely at all at the ordinary temperature, but at 100° the action is complete in eight hours. The hexamethylenetetramine hydrochloride formed was identified by conversion into the dibromide and the nitroso-compound (compare preceding Abstract). JN. W.

Constitution of Hexamethylenetetramine. By R. CAMBIER and A. BROCHET (*Compt. rend.*, 1895, **120**, 105—107).—The authors ascribe to hexamethylenetetramine the constitution $N(CH_2{\cdot}N{:}CH_2)_3$. This formula shows clearly the properties of compound ammonias, explains the easy conversion of the amine into formaldehyde and ammonia in presence of excess of acid, and also explains the action of nitrous acid, which, with excess of the amine, yields carbonic anhydride and dinitrosopentamethylenetetramine, and with excess of the acid yields trinitrosotrimethylenetriamine. The formula indicates the possible formation of additive products of the type $C_6H_{12}N_4R_6$, whilst only the terms R_2 and R_4 are known, but there is evidence that the type R_4 is the limit of additive products of this class. According to the formula, hexamethylenetetramine stands in the same relation to ammonia as the methyleneamidoacetonitrile of Jay and Curtius does to hydrocyanic acid.

The formation of methylamine from the tetramine is not due, as Trillat and Fayollat supposed (Abstr., 1894, i, 64) to hydrogenation, but to a secondary action which will be described later.

C. H. B.

Methanehydrazomethane. By CARL D. HARRIES and E. KLAMT (*Ber.*, 1895, **28**, 503—505).—*Methanehydrazomethane*, NHMe·NHMe, is prepared, like the ethane derivative (Abstr., 1894, i, 568), from lead diformylhydrazine and methylic iodide, the former compound being prepared from normal, not from basic, lead acetate; after purifica-

tion with potash and baryta, the base boils at 50—60°. It is a colourless, highly refractive liquid, fumes strongly in the air, has an unpleasant, amine-like odour, and readily reduces Fehling's solution at the ordinary temperature. The *sulphate* and *hydrochloride* crystallise in deliquescent, colourless plates. The *benzoyl derivative* is insoluble; the *thiosemicarbazide* is crystalline. The *picrate* and *platinochloride* have also been prepared. Compared with ethanehydrazoethane, the methane derivative is more readily prepared, and its compounds crystallise better. J. B. T.

Hydrazides of Monobasic and Dibasic Acids of the Fatty Series. By THEODOR CURTIUS, G. SCHÖFER, and N. SCHWAN (*J. pr. Chem.*, 1895, [2], **51**, 180—196; compare this vol., i, 32).—*Formhydrazide*, $CHO\cdot NH\cdot NH_2$, prepared from ethylic formate and hydrazine hydrate, crystallises in large, transparent, hygroscopic tablets and in long needles, melts at 54°, and is very soluble in alcohol, ether, chloroform, and benzene; it is decomposed by all dilute acids, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. *Benzylideneformylhydrazine*, $COH\cdot NH\cdot N{:}CHPh$, is the product of the condensation of formhydrazide with benzaldehyde; it crystallises in lustrous, white needles, and melts at 134°. *Parahydroxybenzylideneformylhydrazine*, from parahydroxybenzaldehyde and formhydrazide, crystallises in white laminæ, and melts at 243°. *Ethylic formylhydrazoneacetoacetate*, $CHO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot COOEt$, from ethylic acetoacetate and formhydrazide, crystallises in white laminæ, and melts at 91°. *Diformylhydrazine*, $CHO\cdot NH\cdot NH\cdot COH$, is obtained when an excess of ethylic formate is heated at 100—130° with hydrazine hydrate in a sealed tube; also by dissolving iodine in an alcoholic solution of formhydrazide until the liquid is permanently yellow; it crystallises in long, lustrous, colourless prisms, melts at 159—160°, and is freely soluble in water, but only sparingly so in alcohol, and insoluble in ether; it reduces ammoniacal silver nitrate, when warmed with it; it does not restore the colour to bleached magenta solution, nor combine with sodium sulphite, but it yields formylphenylhydrazine with phenylhydrazine.

Acethydrazide, $CMeO\cdot NH\cdot NH_2$, crystallises in colourless, hygroscopic needles, melts at 62°, and dissolves in water and in alcohol; the aqueous solution is neutral, and reduces Fehling's solution when warmed. The *benzylidene* compound crystallises in colourless needles, melts at 134°, and is sparingly soluble in water. *Cyanacethydrazide* has been described (Abstr., 1894, i, 272). *Cyanacetylacetonehydrazine*, $CN\cdot CH_2\cdot CO\cdot NH\cdot N{:}CMe_2$, crystallises in needles, and melts at 152°.

Malonhydrazide, $CH_2(CO\cdot NH\cdot NH_2)_2$, is prepared from ethylic malonate and hydrazine hydrate in molecular proportion; it crystallises in needles and laminæ, melts at 152°, and dissolves sparingly in cold water and dilute alcohol, but not in ether; it is very stable towards dilute acids, its *hydrochloride* being precipitated on the addition of strong hydrochloric acid to its aqueous solution. *Benzylidenemalonylhydrazine*, $CH_2(CO\cdot NH\cdot N{:}CHPh)_2$, crystallises in small, sparingly soluble needles, and melts at 226°. *Parahydroxybenzylidene-*

malonylhydrazine, $CH_2(CO\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH)_2$, is a white crystalline powder which melts at 163°, and dissolves in absolute alcohol. *Cinnamylidenemalonylhydrazine*, $CH_2(CO\cdot NH\cdot N{:}CH\cdot CH{:}CHPh)_2$, is a white powder which melts at 217°, and dissolves in hot, absolute alcohol.

Succinhydrazide, $C_2H_4(CO\cdot NH\cdot NH_2)_2$, crystallises in white, silvery laminæ, melts at 167°, and dissolves in water; it resembles malonhydrazide in general behaviour. The *hydrochloride* was prepared. When succinhydrazide is heated above its melting point, it loses a little water and hydrazine, and then solidifies to a mass which is insoluble in hot water and alcohol. *Benzylidenesuccinylhydrazine*, $C_2H_4(CO\cdot NH\cdot N{:}CHPh)_2$, crystallises in nacreous laminæ, and is more soluble in alcohol than is the malonyl-derivative. *Parahydroxybenzylidenesuccinylhydrazine* is a white crystalline powder which melts at 216°, and dissolves easily in absolute alcohol. *Cinnamylidenesuccinylhydrazine*, $C_2H_4(CO\cdot NH\cdot N{:}CH\cdot CH{:}CHPh)_2$, forms a white powder, melts at 239°, and is very sparingly soluble. *Acetophenonesuccinylhydrazine*, $C_2H_4(CO\cdot NH\cdot N{:}CMePh)_2$, is a white powder, melts at 238°, and is very sparingly soluble in absolute alcohol. When succinhydrazide (1 mol.) is treated with sodium nitrite (2 mols.) and acetic acid, much nitrogen is evolved, and a white precipitate, $C_4H_6N_2O_2$, separates; this is insoluble in most solvents, but soluble in alkalis and in dilute sulphuric acid; it yields a white, silver compound unstable in air.

Oxalhydrazide, $C_2O_2(NH\cdot NH_2)_2$, obtained from ethylic oxalate and hydrazine hydrate, crystallises in long, thick needles which decompose at 235°; it reduces Fehling's solution less easily than do succin- and malon-hydrazide, than which it is less soluble, but which it otherwise resembles. The *hydrochloride* is described. When oxalhydrazide is treated with sodium nitrite and acetic acid, a white compound of the empirical formula $C_2N_2O_2H_2$ is obtained; this appears to be also the product of the action of mercuric oxide on the hydrazide. *Benzylideneoxalhydrazine* crystallises in white laminæ, melts above 250°, and is insoluble in water, and very sparingly soluble in alcohol. *Parahydroxybenzylideneoxalhydrazine* and *cinnamylideneoxalhydrazine* are also sparingly soluble compounds which melt above the boiling point of strong sulphuric acid. A. G. B.

Thiamines. By Felix Lengfeld and Julius Stieglitz (*Ber.*, 1895, **28**, 575—576).—*Tetraethylthiodiamine*, $S(NEt_2)_2$, is prepared from sulphur dichloride and diethylamine; it is a pale yellow, oily liquid with a pleasing smell, and darkens by prolonged exposure to air. It boils at 87—87·5° under a pressure of 19 mm., and at about 190° under the ordinary pressure, part being decomposed. Concentrated acids decompose it immediately, and sulphur is liberated, whereas potash and water act only slowly. Cryoscopic molecular weight determinations agree with the above formula, which indicates that sulphur dichloride is SCl_2 and not $S_2Cl_2 + Cl_2$. J. B. T.

Imido-ethers. By Adolf Pinner (*Ber.*, 1895, **28**, 473—488).—An imido-ether, $R\cdot C(NH)\cdot OR''$, is obtained as hydrochloride by pass-

ing hydrogen chloride into a solution of the cyanide, R·CN, in the alcohol, R″OH. Ammonia converts it into an amidine, $R{\cdot}C(NH){\cdot}NH_2$; a primary amine, NH_2R', and a secondary amine, NHR_2', convert it respectively into a symmetrical and an unsymmetrical substituted amidine, $R{\cdot}C(NR'){\cdot}NHR'$ and $R{\cdot}C(NH){\cdot}NR_2'$. With diazobenzene, the amidine, $R{\cdot}C(NH){\cdot}NH_2$, yields a compound, $R{\cdot}C(NH){\cdot}NH{\cdot}N{:}NPh$; with phenylcarbimide, a diureïde, $NHPh{\cdot}CO{\cdot}N{:}CR{\cdot}NH{\cdot}CO{\cdot}NHPh$, and sometimes also a ureïde, $R{\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}NHPh$; with phenylthiocarbimide, a thiocarbamide, $R{\cdot}C(NH){\cdot}NH{\cdot}CS{\cdot}NHPh$; with ethylic chloroformate, a urethane, $R{\cdot}C(NH){\cdot}NH{\cdot}COOEt$; with carbonyl chloride, a carbamide, $CO[NH{\cdot}CR(NH)]_2$, and then a hydroxycyanidine, $N\lessgtr^{CR{\cdot}N}_{CR{:}N}\gtrgt C{\cdot}OH$; with acetic anhydride and sodium acetate, an acetylamido-derivative, $R{\cdot}CO{\cdot}NHAc$, together with a methylcyanidine, $N\lessgtr^{CR{\cdot}N}_{CR{:}N}\gtrgt CMe$; with derivatives

$$R'{\cdot}C(OH){:}CR''{\cdot}COOEt,$$

of the type of ethylic acetoacetate, hydroxypyrimidines,

$$N\lessgtr^{CR\text{—}N}_{CR'{:}CR''}\gtrgt C{\cdot}OH,$$

are formed; with ethylic oxalacetate, $COOEt{\cdot}C(OH){:}CH{\cdot}COOEt$, it yields a salt of a hydroxypyrimidinecarboxylic acid,

$$N\lessgtr^{CR\text{———}N}_{C(COOEt){:}CH}\gtrgt C{\cdot}OH;$$

and with ethylic acetonedicarboxylate,

$$COOEt{\cdot}CH_2{\cdot}C(OH){:}CH{\cdot}COOEt,$$

a salt of a hydroxypyrimidineacetic acid,

$$N\lessgtr^{CR\text{———}N}_{C(CH_2{\cdot}COOEt){:}CH}\gtrgt C{\cdot}OH.$$

The substances enumerated below were prepared by means of these reactions; the numbers given are melting points, the substances often decomposing at the same time. Many of the derivatives of nitrobenzamidine were converted by reduction into the corresponding amidobenzamidine derivatives.

Starting point, hexylic cyanide.—*Heptenylimidoethers*,

$$C_6H_{13}{\cdot}C(NH){\cdot}OR'';$$

the *hydrochlorides* of the *methyl* (88°), *ethyl* (67°), and *propyl* (70°) ethers are very hygroscopic; those of the *butyl* and *amyl* ethers could only be obtained as a mixture of crystals and syrup; they yield alkylic chloride and œnanthylamide when heated; the free ethers cannot be obtained from them. *Heptenylamidine hydrochloride*, 66°; *platinochloride*, yellow, 157°; *nitrate*, 131°; *chromate*, yellow, 149°; *picrate*, yellow, 152°. *Dimethylheptenylamidine; symmetrical, platinochloride*, 183°; *unsymmetrical; hydrochloride*, 83—84°, *platinochloride*, yellow, 178°. *Heptenyldiphenyldiureïde*, 170° (when boiled with

alcohol, yields heptoylphenylcarbamide, $C_6H_{13}\cdot CO\cdot NH\cdot CO\cdot NHPh$, 89°). *Hexylmethylhydroxypyrimidine*, 82°; *hexyldimethylhydroxypyrimidine*, 102°; *hexylmethylethylhydroxypyrimidine*, 89°; *hexylphenylhydroxypyrimidine*, 167°. *Hexylhydroxypyrimidinecarboxylic acid*, 219°.

Starting point, ethylic cyanacetate.—*Ethylic imidomalonate hydrochloride*, $COOEt\cdot CH_2\cdot C(NH)\cdot OEt,HCl$, 102° (when heated, yields ethylic chloride and *ethylic malonamate*, $COOEt\cdot CH_2\cdot CONH_2$, 50°). *Imidomalonamide* (an amidine, $NH_2\cdot CO\cdot CH_2\cdot C(NH)\cdot NH_2$) *hydrochloride*, decomposes at 150° without melting; *aniline salt* of *diphenylacetamidinecarboxylic acid*, $COONH_3Ph\cdot CH_2\cdot C(NPh)\cdot NHPh$, 223°. *Acetamidomethylhydroxypyrimidine*, 250°; *acetamidophenylhydroxypyrimidine*, 243°.

Phenylhydroxypyrimidineacetic acid, when heated, loses carbonic anhydride, and forms phenylmethylhydroxypyrimidine, melting at 216°; *ethylic salt*, 155°; *silver salt*, with $1H_2O$, at 268° when anhydrous. 1 : 4-*Tolylhydroxypyrimidineacetic acid*, when heated, yields 1 : 4-tolylmethylhydroxypyrimidine, melting at 214°; *ethylic salt*, 164°. *Ethylic β-naphthylhydroxypyrimidineacetate*, 193°. *Ethylic furfurylhydroxypyrimidineacetate*, 164°.

Starting point, 1 : 3-nitrobenzonitrile.—*Metanitrobenzamidinediazobenzene*, brownish-yellow, 160°. *Metanitrobenzenyldiphenyldiureïde*, 173°; *nitrobenzimidophenylureïde*, 157°. *Metanitrobenzimidophenylthiocarbamide*, 169—170°. *Metanitrobenzamidineurethane*, 176°. *Metadinitrodiphenylhydroxycyanidine*, 238—240°. *Acetylnitrobenzamide*, yellowish, 198°; *metadinitrodiphenylmethylcyanidine*, yellowish-brown, 185°. *Metanitrophenylmethylhydroxypyrimidine*, 254°; *metanitrophenyldimethylhydroxypyrimidine*, above 300°; *metanitrophenylmethylethylhydroxypyrimidine*, 263°; *metanitrophenylphenylhydroxypyrimidine*, 271°. *Metanitrophenylhydroxypyrimidinecarboxylic acid*, 260°. *Amidobenzamidine hydrochloride* ($2HCl + H_2O$), 260°; *platinochloride*, decomposes without melting. *Amidobenzamidinediazobenzene*,

$$NH_2\cdot C_6H_4\cdot C(NH)\cdot NH\cdot N{:}NPh.$$

Amidobenzamidine diurethane, $COOEt\cdot NH\cdot C_6H_4\cdot C(NH)\cdot NH\cdot COOEt$, 152—153°. *Amidophenylmethylhydroxypyrimidine*, 177°; hydrochloride ($HCl + 5H_2O$), 265° when anhydrous; *platinochloride* ($H_2PtCl_6 + 2H_2O$) loses $1H_2O$ at 100°, the second at 130—140°. C. F. B.

Ethylenemethylal. By Louis Henry (*Compt. rend.*, 1895, **120**, 107—110).—According to Trillat and Cambier (Abstr., 1894, i, 487), the product of the action of trioxymethylene on ethylene glycol is the methylene derivative of the latter, $CH_2(O\cdot CH_2\cdot CH_2\cdot OH)_2$, and they describe it as a liquid boiling at 74—75°, and only slightly soluble in water. The boiling point of diethylmethylal is about 85°, and since it is improbable that the primary dihydroxyl derivative of this compound would be less volatile, the author has repeated Trillat and Cambier's experiments with trioxymethylene and ethylene glycol. He finds that the product is *ethylenemethylal*, $CH_2<\begin{matrix}O\cdot CH_2\\ |\\ O\cdot CH_2\end{matrix}$, a limpid, mobile liquid with a piquant odour and burning taste, miscible with water in all proportions. It boils at 78° under a pressure of 750 mm.;

sp. gr. = 1·0828 at 3°; vapour density, 2·50, the calculated value for $C_3H_6O_2$ being 2·55, and that for $C_5H_{12}O_4$, 4·69. Ethylenemethylal has the same relation to methylal as ethylene oxide has to methylic ether, and similar differences are observed between their boiling points. In general reactions it is analogous to the ethyleneacetal described by Wurtz. When subjected to repeated distillation, it seems to split up into methylene and ethylene oxides.

The author has obtained the dichlorinated derivative of dihydroxydiethylmethylal, $CH_2(O{\cdot}CH_2{\cdot}CH_2Cl)_2$, by the action of chloromethyl chlorethyl ether, $CH_2Cl{\cdot}O{\cdot}CH_2CH_2Cl$, on glycol monochlorhydrin, the chlorinated ether being obtained by the action of hydrogen chloride on an aqueous solution of methanal in presence of glycol monochlorhydrin.

C. H. B.

Dibromosebacic Acids. By Adolph Claus (*J. pr. Chem.*, 1895, [2], **51**, 335—338).—The dibromosebacic acid obtained by Weger (Abstr., 1894, i, 359) by the action of phosphorus tribromide and bromine on sebacic acid at a low temperature, is quite a different substance from that prepared by Claus and Steinkauler (Abstr., 1888, 133) by the action of bromine alone at 160—170°, and yields a different hydroxy-acid.

A. H.

Amidofumarates. By R. Thomas-Mamert (*Bull. Soc. Chim.*, 1894, [3], **11**, 480—486).—The amidofumaramide from ethylic chlorofumarate is identical with the final product of the action of ammonia on ethylic oxalacetate, and is hydrolysed by dilute acids yielding the diamide of the latter acid. The intermediate product of the action of alcoholic ammonia on ethylic chlorofumarate at the ordinary temperature is *ethylic chlorofumaramate* (m. p. 101°), and not a maleïc acid derivative, as stated by Claus and Voeller (Abstr., 1882, 254). At 100°, the chief product is *ethylic amidofumarate*, a colourless, highly refractive, oily liquid, boiling at 142—143° (20 mm.). This substance is also formed by the action of dry or alcoholic ammonia on ethylic oxalacetate; an intermediate, indefinite, white, curdy product, probably additive, is formed, and is converted by dehydration into the amidofumarate. Ethylic amidofumarate is converted by copper acetate, in presence of alcohol and acetic acid, into *copper ethylic oxalacetate*, which crystallises in transparent, grass-green needles. *Potassium ethylic amidofumarate* crystallises in white plates. Ethylic amidofumarate is converted by aqueous ammonia into a substance forming highly refractive, triclinic crystals, and melting at 102°, possibly ethylic diamidosuccinate.

Jn. W.

Aromatic Acidyltartrates and Anhydrides. By P. Freundler (*Bull. Soc. Chim.*, 1894, [3], **11**, 470—477; compare this vol., i, 174, 210).—The anhydrides are prepared from anhydrous tartaric acid and the acid chloride.

Dibenzoyltartaric acid, $C_2H_2(OBz)_2(COOH)_2 + H_2O$, melts at 130°. The *anhydride* crystallises in needles, and melts at 174°; its specific rotatory power in acetone solution is $[\alpha]_D = +142{\cdot}9°$. *Diphenylacetyltartaric acid*, $C_2H_2(O{\cdot}CO{\cdot}CH_2Ph)_2(COOH)_2$, melts at 95—96°. The anhydride crystallises in clinorhombic plates, and melts at 117·5°;

its specific rotatory power in acetone solution is $[\alpha]_D = +60{\cdot}8°$. *Diphenylpropionyltartaric anhydride* and *diparatoluoyltartaric anhydride* could not be completely purified; the rotatory power of the former in acetone solution is approximately $[\alpha]_D = +38{\cdot}3°$. *Dicinnamoyltartaric anhydride* crystallises in slender, silky needles, and melts and decomposes slightly at 147—148°; its specific rotatory power in acetone solution is $[\alpha]_D = +203{\cdot}2°$.

The rotatory powers of the first three homologues become less dextrogyrate as the series is ascended, in accordance with Guye's law. The high rotatory power of the cinnamoyl derivative may be due to the shortening of the phenylpropionic chain, and consequent diminution of its moment, caused by the ethylene linkage.

The alkylic benzoyl- and toluoyl-tartrates were prepared by the action of hydrogen chloride on an alcoholic solution of the anhydride or acid. The other acidyl tartrates described are hydrolysed by hydrochloric acid, and were prepared by the action of the acid chlorides on the alkylic tartrates; they can be distilled unchanged.

Methylic dibenzoyltartrate crystallises in clinorhombic prisms, sometimes hemihedral, and melts at 132°; the specific rotatory power in alcoholic solution is $[\alpha]_D = -96{\cdot}6°$. The *ethylic* salt melts at 56—58°; the specific rotatory power in alcoholic solution is $[\alpha]_D = -68{\cdot}4°$. The *propylic* and *isobutylic* salts are viscous liquids difficult to purify; the specific rotatory power of the latter in alcoholic solution is $[\alpha]_D = -42{\cdot}9°$.

Methylic diparatoluoyltartrate crystallises in acicular, monoclinic prisms, and melts at 85°; the specific rotatory power in alcoholic solution is $[\alpha]_D = -89{\cdot}1°$.

The diphenylacetyltartrates are highly refractive, viscous liquids, difficult to purify. The *methylic* salt has a sp. gr. = 1·223 at 17°; the specific rotatory power of the liquid at 18° is $[\alpha]_D = +14{\cdot}5°$ that of the alcoholic solution, $[\alpha]_D = +19{\cdot}7°$. The *ethylic* salt has a sp. gr. = 1·174 at 17°; the specific rotatory power of the liquid is $[\alpha]_D = +15{\cdot}3°$, that of the alcoholic solution, $[\alpha]_D = +20{\cdot}2°$. The *propylic* salt has a sp. gr. = 1·143 at 18°; the specific rotatory power of the liquid at 19° is $[\alpha]_D = +20{\cdot}9°$, that of the alcoholic solution $[\alpha]_D = +25{\cdot}2°$.

The rotatory powers of the benzoyl and toluyl derivatives thus vary in accordance with Guye's law, with regard to change both of acidyl and of alkyl groups. The diphenylacetyltartrates should, however, be more lævogyrate than the isomeric diparatoluoyl compounds, and not dextrogyrate as is the case.

The specific rotatory power of solutions of the aromatic acidyl tartrates varies considerably with the nature of the solvent. That of ethylic diphenylacetyltartrate, for example, varies in solutions of the same concentration from +50·1° in carbon disulphide to +22·1° in acetic acid, and +14·0° in benzene. The value in acetone solution, +14·6°, is nearest that of the liquid itself, +15·3°, and does not vary with the concentration. The cryoscopic results obtained with solutions of propylic diphenylacetyltartrate in some of the same solvents were also anomalous, as the author has previously observed in other cases (compare this vol., ii, 194). Jn. W.

Trimethylenepolycarboxylic acids. By EDUARD BUCHNER (*Annalen*, 1895, **284**, 197—212).—This paper contains a classification of some of the properties of trimethylenepolycarboxylic acids, and some interesting considerations regarding their configuration.

M. O. F.

trans-**1 : 2-Trimethylenedicarboxylic acid.** By EDUARD BUCHNER and AUGUST PAPENDIECK (*Annalen*, 1895, **284**, 212—219).—The dimethylic salt of *trans*-1 : 2-trimethylenedicarboxylic acid is obtained by heating methylic pyrazoline-3 : 5-dicarboxylate (Abstr., 1890, 736); the acid forms crystals which belong to the monosymmetric system, $a : b : c = 1{\cdot}8926 : 1 : ?$. $\beta = 59° 00'$. The *calcium* salt forms small crystals, which contain $4\frac{1}{2}H_2O$. A hundred parts of water at 19·5° dissolve 19·69 parts of the acid. The *trans*-acid does not form an anhydride; the silver salt, however, yields the anhydride of the *cis*-modification when heated. The heat of combustion of the *trans*-acid is 479·8 Cals., whilst the value obtained by Stohmann and Kleber for the *cis*-modification is 484·1 Cals. (Abstr., 1892, 1041). *Penicillium glaucum* and *Aspergillus niger* have scarcely any action on either of the isomerides; in this point they resemble 1 : 1-trimethylenedicarboxylic acid, and differ from *cis*-glutaconic acid.

cis-1 : 2-Trimethylenedicarboxylic acid crystallises in large prisms belonging to the monosymmetric system; $a : b : c = 0{\cdot}9435 : 1 : 0{\cdot}4950$. $\beta = 65° 56'$. A hundred parts of water at 20° dissolve 112·9 parts of the acid. When heated with sulphuric acid for three hours at 150°, it is converted into the *trans*-modification, which is also formed by the action of fused potash.

M. O. F.

trans-**1 : 2 : 3-Trimethylenetricarboxylic acid.** By EDUARD BUCHNER and HUGO WITTER (*Annalen*, 1895, **284**, 219—226).—The trimethylic salt of *trans*-1 : 2 : 3-trimethylenetricarboxylic acid is obtained by heating methylic pyrazoline-3 : 4 : 5-tricarboxylate (Abstr., 1888, 1274). The acid crystallises from concentrated aqueous solutions in small needles, and melts at 220°. 106·6 parts are dissolved by 100 parts of water at 9°. The trimethylic salt melts at 59° (compare *loc. cit.*); the *calcium* salt contains $8H_2O$. The *barium* salt contains $1H_2O$; the *copper* and *silver* salts are anhydrous. The *amide* of the dimethylic salt forms colourless needles which melt at 185°. The anhydride, $O<\begin{matrix}CO\\CO\end{matrix}>C_3H_3{\cdot}COOH$, which melts at 189° (*loc. cit.*), is obtained by the action of boiling acetic chloride on the acid, and also by heating the silver salt.

Methylic *cis*-1 : 2-*trans*-1 : 3-trimethylenetetracarboxylate (Abstr., 1885, 1125) melts at 85°. The acid melts at 196—198° (compare *loc. cit.*), with evolution of gas, being converted into *trans*-1 : 2 : 3-trimethylenetricarboxylic acid. Experiments having for their object the preparation of *cis*-1 : 2 : 3-*trans*-1-trimethylenetetracarboxylic acid were unsuccessful.

M. O. F.

Metallic Derivatives of Formylcarbamide, Acetylcarbamide, and Oxaluric acid. By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], **11**, 573—575).—The acidyl derivatives of carbamide form metallic compounds by replacement of amidic hydrogen.

Mercuryformylcarbamide, probably $CHO\cdot N<\overset{CO}{Hg}>NH,H_2O$, is a white precipitate, as is the *silver* compound. *Mercuryacetylcarbamide*, probably $(NHg\cdot CO\cdot NAc)_2Hg$, is decomposed by light. The greater relative amount of mercury is probably due to the increased acidity caused by introduction of the acetyl group. The *silver* and *cuprous* compounds are white. *Basic calcium oxalurate*, probably $CO<\overset{-CO-}{O\cdot Ca}>N\cdot CO\cdot NH_2,H_2O$, is a white, crystalline precipitate.

JN. W.

Salts of Carbamide. By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], **11**, 575—576).—The *acetate* forms tangled, deliquescent crystals, and is insoluble in ether. It dissociates in a dry atmosphere. The heat of formation (sol.) is +1·7 Cal. The *amidoacetate* forms large, brilliant, transparent crystals, and is anhydrous. The heat of formation (sol.) is 0·8 Cal. The *hydrogen malonate*, $C_3O_4H_4,CON_2H_4$, forms large, transparent crystals, and is anhydrous. The heat of formation (sol.) is +2·5 Cal. The normal malonate could not be prepared. The *glycollate* is crystalline, and insoluble in ether. The heat of formation (sol.) is +2·0 Cal. All the above salts are completely dissociated in aqueous solution.

The ureïdes of acetic and amidoacetic acids cannot be formed by direct dehydration of the salts, as the reaction is endothermic; the reverse is the case with the malonate and glycollate. JN. W.

Hydrate of Uric acid. By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], **11**, 571—573).—The heat of formation of dipotassium urate from the acid and dilute potash is +6·5 Cal., and the heat of liberation of the acid from this salt by hydrochloric acid is +21·5 Cal. From these data it follows that the heat of neutralisation of crystallised uric acid is 0·8 Cal. greater than that of precipitated uric acid. Fritzsche's view that the voluminous precipitate liberated by hydrochloric acid from a borax solution of pure uric acid is identical with the crystalline dihydrate obtained in a similar manner from snakes' excrement is therefore confirmed. JN. W.

Action of Hydrazine on Furfurimido-ether. By ADOLF PINNER and N. CARO (*Ber.*, 1895, **28**, 465—473; compare Abstr., 1894, i, 385).—Powdered hydrazine sulphate (1 mol.) is added to the calculated quantity of 33 per cent. caustic potash, furfurimido-ether,

$$C_4H_3O\cdot C(NH)\cdot OEt$$

(1 mol.), is then added, and a little alcohol; after 24 hours, the mixture yields *furfurylhydrazidine*, $C_4H_3O\cdot C(NH)\cdot NH\cdot NH_2$, an oil which solidifies within 12 hours, but then contains some products of decomposition; the *picrate* melts at 164°, and the *benzylidene* compound at 142°. When treated with nitrous acid, it yields *furfuryltetrazotic acid*, $C_4H_3O\cdot C<\overset{N—N}{\underset{NH\cdot N}{\|}}$; this forms crystals, which are usually reddish, but colourless when pure; it melts at 199°, at the same time turning red and decomposing; the *ammonium* salt melts and decomposes at 118°.

If a mixture of the imido-ether with hydrazine, in the proportion of 2 : $1\frac{1}{3}$ mols., is left for 4—5 days, *difurfurylhydrazidine*,

$$[C_4H_3O\cdot C(NH)]_2N_2H_4,$$

is formed. This crystallises in yellow prisms and melts at 185°; the *platinochloride* darkens at 170° and melts and decomposes at 238°. Nitrous acid converts it into *furoylfurfurylhydrazidine*,

$$C_4H_3O\cdot C(NH)\cdot NH\cdot NH\cdot CO\cdot C_4H_3O;$$

this loses water at 120°, forming the triazole. When difurfurylhydrazidine is boiled for half an hour with glacial acetic acid, it yields *difurfuryltriazole*, $C_4H_3O\cdot C\begin{matrix}\diagup N\text{——}\diagdown\\ \diagdown NH\cdot N\diagup\end{matrix}C\cdot C_4H_3O$, which melts at 185°, and yields an *acetyl* derivative melting and decomposing at 120°; it then solidifies, and melts again at 185°.

If the imido-ether and hydrazine, in the proportion of 1 : $1\frac{1}{3}$ mols., are allowed to remain overnight, the mixture filtered, and the filtrate heated on the water bath, *difurfuryldihydrotetrazine*,

$$C_4H_3O\cdot C\begin{matrix}\diagup N\text{——}N\diagdown\\ \diagdown NH\cdot NH\diagup\end{matrix}C\cdot C_4H_3O,$$

is obtained; it forms yellow needles, reddens on exposure to air, and melts and reddens at 208°; the *diacetyl* derivative melts at 197°. It is oxidised on exposure to the air, or by ferric chloride, yielding *difurfuryltetrazine*, $C_4H_3O\cdot C\begin{matrix}\diagup N\cdot N\diagdown\\ \diagdown N:N\diagup\end{matrix}C\cdot C_4H_3O$, which crystallises in red needles, melts at 195°, and is easily reduced to the dihydro-compound. It is converted, by boiling with strong hydrochloric acid, into *difurfurylisodihydrotetrazine*, $C_4H_3O\cdot C\begin{matrix}\diagup N\cdot NH\diagdown\\ \diagdown NH\cdot N\diagup\end{matrix}C\cdot C_4H_3O$, which melts at 245°, and yields a *diacetyl* derivative melting at 166°. If the mixture of imido-ether and hydrazine is at once filtered and the filtrate allowed to remain for 4—6 weeks, *difurfurylimidine*, probably

$$[C_4H_3O\cdot C(NH)]_2NH,$$

is deposited; it is colourless when pure, but is often yellowish, melts at 200°, is a monacid base, and yields only a *diacetyl* derivative, which melts at 138°. C. F. B.

Occurrence of Hexanaphthene in Caucasian Naphtha. By Vladimir B. Markovnikoff (*Ber.*, 1895, **28**, 577—578).—Previous attempts to isolate this compound from Caucasian naphtha have been unsuccessful. A fraction boiling at 78—80° was obtained free from aromatic compounds, having sp. gr. = 0·756 at 15°/15°; this was nitrated, and the portion soluble in potash reduced, when hexamethylenamine was obtained, indicating the presence in the naphtha of hexamethylene (hexanaphthene) in considerable quantity. J. B. T.

Oxidation by Incomplete Combustion. By Johann Walter (*J. pr. Chem.*, 1895, [2], **51**, 107—111).—The author has examined the behaviour of a number of substances when the vapour is mixed

with air and passed over a heated copper spiral, the apparatus being similar to that employed for the preparation of formaldehyde from methylic alcohol. Toluene yields a little benzoic acid, together with benzaldehyde to the extent of 5·7 per cent. of the toluene used up. The best result was obtained by the use of asbestos which had been saturated with ammonium vanadate and ignited; in this case, crystals of impure anthraquinone were also obtained. Phenol, when submitted to the same treatment, yields a little diphenylene oxide. Diphenylamine and methyldiphenylamine yield very small amounts of carbazole and acridine respectively, whilst tolunitrile was obtained from monomethylorthotoluidine. A. H.

Freezing Points of some Carbon Compounds. By RAOUL PICTET (*Compt. rend.*, 1894, **119**, 955—957).—The freezing points of a number of carefully purified carbon compounds were determined, with the precautions previously described.

	Freezing point.		Freezing point.
Benzylic chloride	−47·9°	Piperidine.....	−17·0°
Benzylidenic chloride.	−17·0	Quinoline	−19·5
Benzotrichloride.....	−17·0	Propionic acid	−24·5
Benzaldehyde	−13·5	Ortho-xylene	−45·0
Cinnamaldehyde.....	− 7·5		

Toluene, metaxylene, mesitylene, pyridine, methylaniline, isobutyric acid, and lactic acid do not solidify, even at −100°, and their freezing points are still under investigation.

The introduction of the methyl group into the benzene nucleus always lowers the freezing point; compare benzene and toluene, aniline and methylaniline.

The substitution of chlorine for hydrogen in a methyl group that has been introduced into a benzene nucleus raises the freezing point, but this effect ceases after two chlorine atoms have been introduced.

The results also confirm Baeyer's law that in the case of homologous compounds of similar constitution the freezing point rises and falls according as the number of carbon atoms is odd or even.

The more symmetrical the structure of a compound, and the more compact the grouping of the atoms in the molecule, the higher is the freezing point, as compared with other compounds of the same series; for instance, butyric acid solidifies at −19°, but isobutyric acid does not solidify even at −100°, and normal caproic acid solidifies at −18°, whereas isocaproic acid does not solidify at −100°. The three xylenes are examples of the same law. C. H. B.

α-Hexachlorophenol. By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1894, [3], **11**, 557—560).—α-Hexachlorophenol can be prepared by the action of chlorine on phenol in presence of antimonic chloride. The phenol should first be converted into its trichloro-derivative by the action of chlorine alone, and further chlorination effected in presence of the antimonic chloride (4—5 per cent.) at a temperature not exceeding 125—130°. The mass becomes solid from formation of

pentachlorophenol, and is converted into the liquid hexachloro-derivative by the continued action of the chlorine. If the chlorination is carried too far, an *octochlorophenol* (*hexachlorophenol dichloride*) is formed.

α-Hexachlorophenol, C_6Cl_6O, after crystallisation from benzene and light petroleum, melts at 107°. JN. W.

Bromine Derivatives of Paraisobutylphenol. By FRANK B. DAINS and I. R. ROTHROCK (*Amer. Chem. J.*, 1895, **17**, 113—114).—*Bromoparaisobutylphenol*, prepared by the action of bromine (1 mol.) on the phenol or its sodium salt, crystallises in fan-like clusters of blunt needles, melts at 50°, and is easily soluble in ordinary organic solvents. The *benzoate* yields needles melting at 78·5°. When 2 mols. of bromine or an excess is used, *dibromoparaisobutylphenol* is formed. It crystallises in large, yellow plates, melts at 78°, and is readily soluble in organic solvents. L. T. T.

Identity of Liebmann's Isoamylphenol with Tertiary Amylphenol. By RICHARD ANSCHÜTZ and H. BECKERHOFF (*Ber.*, 1895, **28**, 407—410).—The tertiary amylphenol of B. Fischer and Grützner (Abstr., 1893, 563) is shown to be identical with the isoamylphenol of Liebmann (Abstr., 1882, 171, 727). The former boils at 127·6° under 12 mm. pressure, the latter at 130·6° under 12 mm.; both melt at 93°, and are identical in appearance. Both yield an identical *benzoate* (compare Kreysler, Abstr., 1885, 1055), which melts at 60° (not 80·5—81°), boils at 205° under 11 mm. pressure, and crystallises in the rhombic system; $a : b : c = 0·7209 : 1 : 0·8841$; $2E = 61°\ 30'$ (Li); $62°\ 11'$ (Na); $56°\ 59'$ (Tl). The two substances are therefore identical; probably it is *tertiary* amylphenol. C. F. B.

Nitration of Organic Bases. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 399—403).—This nitration in the side chain can be effected by means of nitric anhydride, but also by the dehydrating action of acetic anhydride on the nitrate of the base; the resulting nitramine ("diazoacid") is converted by mineral acids into a nitro-derivative of the base; for example,

$$C_6H_5·NH_2,HNO_3 \rightarrow C_6H_5·NH·NO_2 \rightarrow NH_2·C_6H_4·NO_2.$$

As regards the yield of nitramine, it is greatest—from 75 per cent. of the base downwards—in the case of ortho- and para-nitro-derivatives, least in the case of bases which, like aniline and toluidine, contain no negative substituting group. The following compounds were prepared; the temperatures given are melting points.

Phenylnitramine, $C_6H_5·NH·NO_2$. *Tolylnitramines*, 1 : 4, white nacreous plates, 52°; 1 : 2, colourless oil. *Nitrophenylnitramines*, 1 : 4, yellow, silky needles, 111—112°; 1 : 3, yellow needles, 86—87°; 1 : 2, lustrous, yellow needles, with sweet taste, 65·5°. *Metanitroparatolylnitramine*, lustrous yellow needles, 79—80°. *Metanitroorthotolylnitramine*, lustrous yellow needles, 103°. *Parachlorophenylnitramine*, lustrous white needles, 107—108°. *Parabromophenyl-*

nitramine, silky white needles, 101·5—102°. *Pseudocumylnitramine*, [$Me_3 : NH{\cdot}NO_2 = 1 : 3 : 4 : 5$], white nacreous needles, 86·5—87°. C. F. B.

Phenylethylenediamine. By Franz Feist and Hugo Arnstein (*Ber.*, 1895, **28**, 425—427; compare A. Purgotti, *Gazzetta*, 1894, ii, 427).—Phenylethylenediamine is obtained by reducing phenylglyoxime with sodium and alcohol. It is a yellow liquid which boils at 243—246°, and absorbs carbonic anhydride more readily than does diphenylethylenediamine. The *carbamate* is a white powder which melts and evolves gas at 155°; the *picrate* forms yellow crystals which melt at 160°. The *dibenzoyl* derivative melts at 217°, and yields a *trinitro*-derivative melting at 117°. M. O. F.

Theory of Diazo-compounds. By Eugen Bamberger (*Ber.*, 1895, **28**, 444—449).—The author holds the view that in diazo-salts the nitrogen atom to which a negative ion is attached must be regarded as quinquevalent. According to this hypothesis, the conversion of diazo- into isodiazo-compounds depends on the transformation of the radicle "phenylazonium" (N:NPh·) into the "phenylazo"-radicle (·N:NPh), in consequence of a more positive ion replacing a negative group. Phenylazonium is, therefore, a positive radicle occurring in normal diazo-salts, normal diazo-hydrates, and in Hantzsch's unstable potassium benzenediazosulphonate; the stable salt contains the phenylazo-radicle, which is also present in azo- and diazoamido-compounds, and in the isodiazo-hydrates and their salts. M. O. F.

The Isomeric Diazobenzene Potassium Sulphites. By Adolph Claus (*J. pr. Chem.*, 1895, [2], **51**, 80—90; compare Abstr., 1894, i, 597).—A polemical paper dealing with the theory of the constitution of these compounds proposed by Hantzsch. (See also this vol., i, 25, 180.) A. H.

Action of Ethylic Cyanacetate on Mononitrodiazobenzene Salts. By Paul W. Uhlmann (*J. pr. Chem.*, 1895, [2], **51**, 217—234).—In order to investigate the influence of substituent groups on the isomerism of the compounds obtained by Krückeberg (Abstr., 1894, i, 369), the author has examined the products of the action of ethylic cyanacetate on the three nitrodiazobenzene chlorides.

The compounds obtained exhibit relations similar to those previously described.

Metanitrodiazobenzene chloride yields the *α-condensation product* as a dark yellow, crystalline powder, which, after recrystallisation from benzene, forms dark brown, lustrous needles, and melts at 136—137°. When it is melted, it passes into the *β-derivative*, which may also be obtained by decomposing the potassium salt with carbonic anhydride, as a light brown, microcrystalline powder melting at 124—125°. Only one *potassium* salt appears to be formed; it crystallises in light brown needles, and, when decomposed by hydrochloric acid, yields the α-derivative, whilst the β-derivative is precipitated by carbonic anhydride. The *sodium* salt crystallises in plates of the same colour as the crystals of the potassium salt. Ethylic iodide reacts with the

potassium salt to form an *ethyl* derivative, which crystallises in long, silky needles melting at 148—149°. Benzoic chloride produces the *benzoyl* derivative which forms almost white, lustrous plates melting at 174—175°. Carbonyl chloride reacts with 2 mols. of the potassium salt to form a substance which melts at 141—142°. When the ethyl derivative is heated with hydrochloric acid at 120—130°, it yields metanitroethylaniline, so that the stable (β) condensation product must be considered as a hydrazone.

The *α-derivative* of paranitrodiazobenzene chloride forms slender, pale yellow needles melting at 170—172°, whilst the *β-derivative*, obtained in a manner similar to the corresponding meta-compound, melts at the higher temperature of 184°, and is a light yellow, granular powder. The potassium salt could not be obtained pure, but forms a violet-red solution. The *α-condensation product* of orthonitrodiazobenzene chloride crystallises in scale-like forms and melts at 116°. When heated to 160°, it is converted into the *β-modification*, which crystallises in large, monosymmetric prisms melting at 146°. The *potassium* salt forms a dark red solution, and crystallises in violet-brown plates with a metallic lustre. The isomeric modifications of all three derivatives also differ in solubility in benzene. A. H.

Explosiveness of 1 : 4-Nitrodiazobenzene Nitrate. By Eugen Bamberger (*Ber.*, 1895, **28**, 538—539).—This substance on one occasion unaccountably exploded with terrible consequences, when it was being brushed along with a porcelain spatula. Generally speaking it is much less explosive than diazobenzene, and has many times been rubbed on a porous tile without exploding. 1 : 4-Nitroisodiazobenzenehydroxide is also explosive, but less violently so.

C. F. B.

Diazobenzene Aniline Chloride. By J. H. Kastle and B. C. Keiser (*Amer. Chem. J.*, 1895, **17**, 91—98).—When attempting to obtain diazobenzene chloride by the action of nitrosyl chloride on aniline hydrochloride, the double salt *diazobenzene aniline chloride*, N_2PhCl,NH_3PhCl, was obtained in the form of well-defined needles which turned green, then pink, and finally brown, when exposed to the air. This salt dissolves freely in alcohol, and in water, yielding green solutions which change to red on boiling or exposure to air. It explodes a little above 105°, and when boiled with water, it evolves two-thirds of its nitrogen and forms phenol and aniline hydrochloride. When reduced with stannous chloride, it yields phenylhydrazine and aniline hydrochloride, and when treated with potash, diazoamidobenzene is formed. It yields a platinochloride, $N_2PhCl,NH_3PhCl,PtCl_4$.

L. T. T.

Synthesis of Aromatic Hydrazines from Hydrazine Hydrate. By Attilio Purgotti (*J. pr. Chem.*, 1895, [2], **51**, 111—112).—The author draws attention to the fact that he described the preparation of 2 : 4-dinitro- and 2 : 4 : 6-trinitro-phenylhydrazine from hydrazine hydrate (this vol., i, 27) before the publication of the paper in which Curtius and Dedichen (this vol., i, 29) described the preparation of the same compounds by the same method. A. H.

Acid Hydrazides and Azides. By THEODOR CURTIUS (*Ber.*, 1895, **28**, 522—523).—In connection with Wolff's recent communication on compounds from acid hydrazides and sugars (this vol., i, 216), the author points out that the first of these substances, arabinose-nitrobenzoylhydrazide, was prepared by Radenhausen, and that he himself, and not Struve, prepared and described benzoylhydrazide in 1890. He desires to reserve the acid hydrazides and azides for further uninterrupted investigation. J. B. T.

Mononitrobenzoylhydrazines. By THEODOR CURTIUS and O. TRACHMANN (*J. pr. Chem.*, 1895, [2], **51**, 165—179; compare this vol., i, 32).—*Methylic orthonitrobenzoate* is a yellow liquid which has an odour of strawberries, and boils at 275°; a similar odour has been ascribed to the meta-compound, but when pure this has no odour.

Orthonitrobenzoylhydrazine, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2$, is obtained by the interaction of methylic orthonitrobenzoate, with the calculated quantity of hydrazine hydrate; it crystallises in large, long, yellow prisms, melts at 123°, and dissolves somewhat freely in alcohol and water, but not in ether, &c.; it reduces Fehling's solution and ammoniacal silver nitrate very quickly; dilute mineral acids decompose it into its parent compounds. *Metanitrobenzoylhydrazine*, similarly prepared, crystallises in yellow needles, melts at 152°, and is less soluble than the ortho-compound, which it otherwise resembles. *Paranitrobenzoylhydrazine* crystallises in slender, yellow needles, melts at 210°, and is less soluble than the other two isomerides, which it resembles in chemical behaviour. The *sodium* derivatives, $NO_2 \cdot C_6H_4 \cdot CO \cdot NNa \cdot NH_2$, and the *hydrochlorides*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2,HCl$, of the three isomerides are described.

Benylidene-ortho-, -meta- and -para-nitrobenzoylhydrazine,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot N{:}CHPh,$$

prepared by the interaction of benzaldehyde and the nitrobenzoylhydrazines, are described; they melt at 152°, 203°, and 247°, respectively. With acetone, the nitrobenzoylhydrazines yield *acetone-nitrobenzoylhydrazines*, $CMe_2{:}N \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$; the *ortho*-derivative forms yellow crystals, and melts at 205°; the *meta*-derivative small, yellow crystals, and melts at 152°; the *para*-derivative crystallises in greenish-yellow needles; they dissolve in alcohol.

The *ethylic nitrobenzoylhydrazoacetoacetates*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot N{:}CMe \cdot CH_2 \cdot COOEt,$$

are obtained by the interaction of the nitrobenzoylhydrazines with ethylic acetoacetate; the *ortho*-derivative crystallises in lustrous, yellow prisms, melts at 113°, and dissolves freely in alcohol and chloroform; the *meta*-derivative forms small, white crystals, melts at 106°, and dissolves freely in alcohol; the *para*-derivative is rather more difficult to prepare, and crystallises in aggregates of yellow needles, freely soluble in alcohol.

Dinitrodibenzoylhydrazines, $N_2H_4(CO \cdot C_6H_4 \cdot NO_2)_2$, are formed by heating the ethylic nitrobenzoylhydrazine acetoacetates above their melting points, or by dissolving them in dilute alkalis, and warming the

solutions with an excess of acid. The *di-ortho*-compound crystallises in slender, white needles or laminæ, melts above 250°, and is freely soluble in hot glacial acetic acid; the *di-meta*-compound crystallises in white laminæ or needles, melts at 242°, and is freely soluble in hot glacial acetic acid; the *di-para*-compound forms yellowish, slender needles, melts above 245°, and is also freely soluble in hot glacial acetic acid. The dinitrodibenzoylhydrazines are soluble without appreciable decomposition in solutions of the alkalis, and if the calculated quantities be employed alkali derivatives are obtained. They show no tendency to form nitroso-derivatives or acetyl derivatives; acids convert them into nitrobenzoic acids and hydrazine salts.

A. G. B.

Imido-derivatives of Carbonic acid. By FELIX LENGFELD and JULIUS STIEGLITZ (*Amer. Chem. J.*, 1895, **17**, 98—113).—*Bromo-formanilide*, NHPh·COBr, was formed by passing dry hydrogen bromide over phenylic isocyanate. It forms white crystals, melts at 67°, and decomposes into its components at 85—100°. Hydrogen chloride appears to be without action on bromo-formanilide, and hydrogen bromide without action on chloro-formanilide. *Phenylimidocarbonyl bromide*, NPh:CBr_2, was prepared by the action of bromine on phenylic isocyanide. It is an oil boiling at 127° under 18 mm. pressure. When treated with sodium ethoxide, it yields *ethylic phenylimidobromoformate*, NPh:CBr·OEt, which decomposes on boiling and is less stable than the corresponding chloro-derivative. When acted on by hydrochloric acid, it mainly yields chloro-formanilide and ethylic bromide, although a small quantity of bromo-formanilide and ethylic chloride is produced, and a very similar product is yielded by the action of hydrogen bromide on ethylic phenylimidochloroformate. The constitution of the intermediate additive compounds probably formed is discussed, but the authors did not succeed in isolating them. When, however, phenylic phenylimidochloro-formate is treated with hydrogen chloride, the additive product *phenoxyformophenylamido-dichloride*, OPh·CCl_2·NHPh, can be isolated as a white substance softening at 60° and melting at 65°. In the presence of moisture, it forms phenyl carbanilate.

When carbodiphenylimide is treated with hydrogen chloride, the hydrochloride $C(NPh)_2$,HCl (m. p. 92—95°) is first formed, and then *carbodiphenylimide dihydrochloride*, $C(NPh)_2$,2HCl. This crystallises in tetragonal or orthorhombic prisms, and begins to melt and decompose at 130°, apparently leaving a carbodiphenylimide. When boiled with water, it gives carbanilide.

When chloro-formodiphenylamidine, NHPh·CCl:NPh, is treated with sodium ethoxide, ethoxyformodiphenylamidine, NHPh·C(OEt)·NPh, is formed, and this with hydrogen chloride yields ethylic chloride and carbanilide $CO(NHPh)_2$.

The results show that when hydrogen chloride is taken up by acid derivatives of the formula OR·CX:NPh or Y″:C:NPh, containing the phenylimido-group, the double linking is severed and the group :CCl·NHPh formed.

L. T. T.

Action of Sodium Ethoxide on Carbodiphenylimide. By JULIUS STIEGLITZ (*Ber.*, 1895, **28**, 573—574).—*Ethylisocarbanilide*

(ethylic phenylimidocarbanilate), HNPh·C(NPh)·OEt, is prepared by the interaction of carbodiphenylimide and sodium ethoxide in alcoholic solution at −5°; it is a colourless mobile liquid, boiling at 182° (10 mm.), the refractive index = 1·6028 at 20°. The yield is practically quantitative. From the production of similar compounds to the above by the action of sodium ethoxide on carbodiphenylimide chloride, the author and F. Lengfeld (preceding abstract) recently concluded that the latter compound has the formula HNPh·CCl:NPh; this now requires confirmation or revision, and the subject is being further investigated. J. B. T.

Constitution of Rosaniline. By LOTHAR MEYER (*Ber.*, 1895, **28**, 519—522).—Referring to Weil's paper on the constitution of triphenylmethane derivatives (this vol., i, 234), the author points out that a photometric investigation of the products formed by the action of hydrochloric acid on magenta has been in progress under his direction for more than 10 years. With hydrochloric acid, aqueous or alcoholic, in excess, yellowish red hydrochlorides are formed; when diluted, these change successively to colourless compounds, and finally to blue-red magenta. These results are in better accord with Rosenstiehl's formula for rosaniline than with E. and O. Fischer's, which indicates the presence of a quinoidal linkage (compare Abstr., 1893, i, 464). If the first formula is correct, then the yellowish-red compound is probably the chloride $CCl(C_6H_4\cdot NH_2,HCl)_3$, the colourless substance is the carbinol $HO\cdot C(C_6H_4\cdot NH_2,HCl)_3$, and the blue-red one the chloride $CCl(C_6H_4\cdot NH_2)_3$. The subject is being further investigated in various directions. A number of crystalline ethers has been prepared from triphenylbromomethane and metallic alkyloxides, and will be described later. J. B. T.

Preparation of Condensation Products from Chloroform and Benzene. By GUSTAV WENDT (*J. pr. Chem.*, 1895, [2], **51**, 344—346).—The amount of condensation product obtained in the preparation of flavaniline from acetanilide and of triphenylmethane from chloroform and benzene is largely increased by the addition of kieselguhr, whilst sand has no marked effect on the yield. A. H.

Constitution of the Safranines. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 508—513; compare this vol., i, 219).—Dinitrodimethylmetamidodiphenylamine, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot NMe_2$, is prepared from 1 : 2 : 4-chlorodinitrobenzene and metamidodimethylaniline hydrochloride; it crystallises from alcohol in garnet-red plates, and melts at 136—137°. The *nitroso*-derivative is deposited in scarlet flocks. *Dinitrotetramethylsafranine* is prepared by the oxidation of a mixture in molecular proportion of dinitrodimethylmetamidodiphenylamine and paramidodimethylaniline sulphate, a blue compound is first formed, which when heated is converted into the safranine.

Dinitrophenylphenylene-blue,

$$\overset{3}{N}H:\overset{6}{C_6H_4}:\overset{}{N}\cdot\overset{3}{C_6H_3}(\overset{}{N}H_2)\cdot\overset{1}{N}H\cdot\overset{2:4}{C_6H_3}(NO_2)_2,$$

is obtained in a similar manner from dinitrometamidodiphenylamine

and phenylenediamine hydrochloride, as a blue, crystalline powder with a coppery reflex; it is insoluble in water, is readily converted into the safranine when exposed to air in alcoholic solution, explodes when heated and decomposes and becomes yellow by the action of mineral acids.

The *safranine*, $NH_2 \cdot C_6H_3 < \begin{matrix} N:C_6H_3:NH \\ | \\ -N \cdot C_6H_3(NO_2)_2 \end{matrix}$, is prepared by heating the preceding indamine in alcoholic solution. The *hydrochloride* dissolves in water and alcohol with a carmine, in concentrated hydrochloric acid with a sky blue, and in concentrated sulphuric acid with a green coloration; with cotton mordanted with tannin, it gives a bluer lustre than "safranine T," and is deposited in greenish lustrous crystals. The *diazo-derivative* is violet-blue.

The formation of safranines as described above, resembles the conversion of tolylene-blue into tolylene-red which contains two amido-groups and the complex $< \begin{matrix} N \\ | \\ N \end{matrix} >$, whilst the safranines probably contain a quinoidal linkage; it is to this that the difference in their behaviour, especially in their basic properties, is due. That phenosafranine does not contain two amido-groups is proved by its yielding in aqueous solution a monodiazo-derivative only, not a tetrazo-compound like tolylene-red, therefore it cannot be an ammonium base. Safranide, formed by boiling diazophenosafranine in alcoholic solution, yields no diazo-compound, it therefore contains no amido-group, and cannot be an ammonium base. J. B. T.

Orthocoumaraldehyde Methyl Ether from Oil of Cassia. By JULIUS BERTRAM and RUDOLF KÜRSTEN (*J. pr. Chem.*, 1895, [2], **51** 316—325).—Oil of Cassia often yields a crystalline product on rectification. This consists of *orthocoumaraldehyde methyl ether*,

$$MeO \cdot C_6H_4 \cdot CH:CH \cdot CHO,$$

and forms large, faintly yellowish crystals which melt at 45—46°. It boils at 160—161° (12 mm.) and decomposes very readily when exposed to light and air. The *phenylhydrazone* forms pale yellow crystals melting at 116—117°, and the *oxime* crystallises in colourless matted needles melting at 125—126°. The constitution of the aldehyde follows from the facts, that when fused with potash it is converted into salicylic acid, that it is oxidised by potassium permanganate to methylsalicylic acid, $OMe \cdot C_6H_4 \cdot COOH$, and that silver oxide converts it into β-methylcoumaric acid, $MeO \cdot C_6H_4 \cdot CH:CH \cdot COOH$, melting at 182—183°. It can readily be prepared synthetically by the condensation of methylsalicylaldehyde with acetaldehyde.

β-Methylcoumaric acid undergoes polymerisation when exposed to light, an acid which has a molecular weight of 356 and which melts at 260—262° being formed. Cinnamic acid also undergoes partial polymerisation under the same circumstances, an acid which melts at 274°, and is probably identical with Liebermann's α-truxillic acid, being formed. A. H.

Dihydromethylcoumaran. By CARL D. HARRIES and GEORGE J. BUSSE (*Ber.*, 1895, **28**, 501—503).—Methyl orthohydroxystyrylketone

(methylorthocoumaroketone), $HO\cdot C_6H_4\cdot CH{:}CH\cdot COMe$, prepared from salicylaldehyde and acetone, yields *methyl orthohydroxydihydrostyryl ketone* (methyldihydrocoumaroketone), $HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COMe$, not methylorthocoumaryl alcohol, $HO\cdot C_6H_4\cdot CH{:}CH\cdot CHMe\cdot OH$, as previously stated (Abstr., 1892, 169). The *phenylhydrazone* melts at 123—124°. The ketone, when reduced with zinc and hydrochloric acid, is converted into *dihydromethylcoumaran*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ O-CHMe\end{matrix}$, a derivative of the complex $C_6H_4<\begin{matrix}CH_2\cdot CH\\ O-CH\end{matrix}$, for which the name *coumaran* is proposed. It is a colourless highly refractive liquid with a pleasing smell, readily miscible with ordinary media, boils at 223—226° (76 mm.), and gives a red coloration with sulphuric acid.

J. B. T.

Reactions of Amidobenzoic acids. By William Oechsner de Coninck (*Compt. rend.*, 1895, **120**, 100—101).—Alkali hypochlorites produce, with orthoamidobenzoic acid, a red coloration; with the *meta*-acid a red-brown; with the *para*-acid an orange-red; alkali hypobromites produce a bright orange-red colour with all three acids. Alkali hypoiodites give an orange-red with the *ortho*-acid, deep orange or yellow with the *meta*-acid, bright orange or yellow with the *para*-acid; calcium hypochlorite with the *ortho*-acid produces a deep violet coloration which rapidly becomes black or dark green; with the *meta*-acid and the *para*-acid it gives a yellowish-brown coloration. Ferric chloride in very dilute solution gives with the *ortho*-acid a rose colour which changes to wine-red; with the *meta*-acid an amber-yellow, and with the *para*-acid a red-brown colour.

The nitrobenzoic acids give no reactions with these reagents. The reactions with the amido-acids are much more rapid and sensitive than those previously described (Abstr., 1892, 847, 1380; 1893, i, 413, 465, 641).

C. H. B.

Action of Bromine on Phenylic Salicylate, Phenylic Benzoate, Ortho-, Meta-, and Para-Cresylic Benzoate, and Guiacol Benzoate. By P. Kauschke (*J. pr. Chem.*, 1885, [2], **51**, 210—213).—Phenylic bromosalicylates are produced by the direct bromination of salol, but the tribromo-derivative in small quantity only unless the reaction be conducted at 100°, under pressure, and in the presence of iodine or ferric chloride. The monobromosalicylate,

$$[COOH : OH : Br = 1 : 2 : 5],$$

melts at 111·5°, and its *amide* at 232°. The dibromosalicylate, $[COOH : OH : Br_2 = 1 : 2 : 3 : 5]$, melts at 126°, and its amide at 170°. These have been described before.

Phenylic tribromosalicylate, $[COOH : OH : Br_3 = 1 : 2 : 3 : 5 : ?]$, crystallises in long needles, melts at 192°, and dissolves in chloroform and glacial acetic acid; its *amide* melts at 97°. *Bromophenylic tribromosalicylate*, $OH\cdot C_6HBr_3\cdot COO\cdot C_6H_4Br$, crystallises in needles, melts at 164°, and is sparingly soluble in glacial acetic acid and in chloroform.

Bromophenylic benzoate is the product of the action of bromine (1 or 2 mols.) on phenylic benzoate (1 mol.); it melts at 102°. By the action of a larger proportion of bromine, the *compound* $C_{12}H_3Br_7O_4$ is formed; this crystallises in golden laminæ, melts at 260°, and is sparingly soluble; it is reduced by sulphurous acid to a white substance of the formula $C_{12}H_5Br_7O_4$, indicating its probable quinonoid character.

Bromorthocresylic benzoate melts at 59°; *bromometacresylic benzoate* at 82°; *bromoparacresylic benzoate* is a yellow oil which solidifies to long needles, below 0°. *Bromoguiacol benzoate* crystallises in colourless prisms and melts at 76—78°. A. G. B.

Cadmium Salicylate. By P. Cæsaris (*L'Orosi*, **17**, 262—265).—*Cadmium salicylate*, $(C_7H_5O_3)_2Cd$, prepared by ordinary methods, using the acid and cadmium oxide or carbonate, is obtained in lustrous crystals melting at 300°; it is sparingly soluble in water, but more soluble in alcohol, ether, or glycerol. The salt possesses valuable antiseptic properties. W. J. P.

Phenyl-α-amidolactic acid (Phenylserine). By Emil Erlenmeyer, jun., and Ernst Früstück (*Annalen*, 1895, **284**, 36—49; compare Abstr., 1893, i, 166).—Among the condensation products obtained from benzaldehyde and glycocine in presence of sodium hydroxide, is the *sodium* salt of α-benzylideneamidophenyllactic acid,

$$OH\cdot CHPh\cdot CH(N{:}CHPh)\cdot COONa.$$

The acid itself has not been isolated, but its *acetyl* derivative crystallises in needles and melts at 169—170°.

Anhydrous phenyl-α-amidolactic acid decomposes below 190°; the hydrated acid, which contains $1H_2O$, melts at 193—194° with decomposition. The *copper* salt is violet. Benzoic anhydride converts phenylamidolactic acid into the lactimide of benzoylamidocinnamic acid, $CHPh{:}C<\begin{matrix}CO\\|\\NBz\end{matrix}$, which is also obtained by condensing benzaldehyde with hippuric acid. The lactimide, $CHPh{:}C<\begin{matrix}CO\\|\\NAc\end{matrix}$, produced by the action of acetic anhydride on phenyl-α-amidolactic acid, crystallises from alcohol in white needles which melt at 146—147°; it is also obtained by the condensation of benzaldehyde with glycocine in presence of acetic anhydride. When the solution of the lactimide in sodium hydroxide is acidified, the *acetyl* derivative of α-amidocinnamic acid is formed; it crystallises from water and contains $2H_2O$. The hydrated acid melts at 185—186°, and the anhydrous substance melts and evolves gas at 190—191°. M. O. F.

Nitrophenylglycidic acids. By Alfred Einhorn and Alfred Gernsheim (*Annalen*, 1895, **284**, 132—153; compare Eichengrün and Einhorn, Abstr., 1890, 1128).—The acid obtained (*loc. cit.*) on oxidising orthonitrometachlorophenyl-β-lactaldehyde and orthonitrometachlorophenylhydroxyethyl methyl ketone melts at 156°. It was

at first supposed that this acid was nitrochlorophenyl-β-lactic acid, but the results of the author's experiments now show that on oxidising a substituted phenyllactaldehyde or methyl ketone with sodium hypochlorite, the corresponding phenylglycidic acid is formed. The acid (m. p. 156°) prepared from nitrochlorophenylhydroxyethyl methyl ketone is, therefore, the nitrochlorophenylglycidic acid, $O<\begin{matrix}CH\cdot C_6H_3Cl\cdot NO_2\\ |\\ CH\cdot COOH\end{matrix}$. By means of this reaction, orthonitrophenylglycidic and 3 : 6-bromonitrophenylglycidic acids have been prepared.

Metabromobenzaldehyde forms an *oxime* which melts at 71·5°; the *phenylhydrazone* melts at 141—142°.

3 : 6-*Bromonitrobenzaldehyde* crystallises from alcohol in long, pale yellow needles, and melts at 74°; it dissolves in hot water, and is volatile in an atmosphere of steam. The *phenylhydrazone* forms dark red needles which melt and decompose at 180°; the *oxime* crystallises from water in pale yellow needles, and melts at 113°.

3 : 6-*Bromonitrophenylhydroxyethyl methyl ketone*,

$$NO_2\cdot C_6H_3Br\cdot CH(OH)\cdot CH_2\cdot COMe,$$

is prepared by the action of aqueous soda on a solution of bromonitrobenzaldehyde in acetone. It crystallises from alcohol in lustrous plates, and melts at 101—102°; alkalis convert it into dibromindigo, and the solution in concentrated sulphuric acid is red.

3 : 6-*Bromonitrophenylglycidic acid* is obtained by agitating the foregoing compound with an aqueous solution of sodium hypochlorite at 70—80°. It crystallises from dilute alcohol in small, lustrous, pale yellow plates which melt at 156°; at this temperature, the substance decomposes and becomes blue, owing to the formation of dibromindigo. The *potassium* salt crystallises from dilute alcohol in lustrous needles; the *barium* and *calcium* salts crystallise from hot water.

3 : 6-*Bromonitrocinnamic acid* is formed when bromonitrobenzaldehyde is heated with acetic anhydride and anhydrous sodium acetate for 7—8 hours at 140—150. It crystallises in lustrous needles and melts at 171°; the solution in concentrated sulphuric acid is green. The *silver* salt is crystalline.

3 : 6-*Bromonitrophenyl-α-chlorolactic acid* is obtained by treating the potassium salt of the foregoing acid with sodium hypochlorite; it melts at 147—148°. Alcoholic potash converts it into bromonitrophenylglycidic acid.

3 : 6-*Bromonitrophenyl-β-lactaldehyde*,

$$NO_2\cdot C_6H_3Br\cdot CH(OH)\cdot CH_2\cdot COH,$$

is prepared by agitating a solution of bromonitrobenzaldehyde in acetaldehyde with aqueous soda; it crystallises with 1 mol. acetaldehyde, which is lost at 87°. This compound melts and becomes green at 92—93°; alkalis convert it into dibromindigo. The *phenylhydrazone* crystallises from alcohol in dark red needles, and melts at 201°. Sodium hypochlorite oxidises the aldehyde to bromonitrophenylglycidic acid, whilst silver oxide converts it into 3 : 6-*bromonitrophenyl-β-lactic acid*. This crystallises from hot water in slender silky needles, and melts at 152°; the *silver* salt is crystalline and

the *copper* salt forms dark blue needles. The *ethylic* salt separates from light petroleum in large crystals, and melts at 74·5°.

M. O. F.

Acetylgallic and Acetyldibromogallic acids. By PAUL SISLEY (*Bull. Soc. Chim.*, 1894, [3], **11**, 563—568).—Dry acetic chloride has no action on gallic acid, and the product obtained in presence of a trace of water cannot be purified satisfactorily (compare Biétrix, Abstr., 1894, i, 130). When, however, gallic acid is heated with acetic anhydride, and the partially purified product again subjected to the same treatment, *triacetylgallic acid* is obtained as a white, amorphous substance, which crystallises from boiling toluene in very light, colourless, prismatic needles containing toluene of crystallisation. The anhydrous substance melts at 151°. It is insoluble in water, but is slowly hydrolysed by it to diacetylgallic acid. The alcoholic solution does not give a colour reaction with ferric chloride.

Diacetylgallic acid, with $\frac{1}{2}H_2O$, melts at 162°. In alcoholic solution it gives a yellow precipitate with ferric chloride, but no colour reaction, so that the presence of at least two phenolic groups in the gallic acid molecule appears to be necessary for this purpose. It does not give precipitates or colorations with lime-water or alkalis, or with uranium nitrate. Attempts to prepare the monacetyl compound were unsuccessful.

Triacetyldibromogallic acid, from dibromogallic acid, crystallises from toluene in white, prismatic needles, and melts at 168°, not at 94—98°, as stated by Biétrix (*loc. cit.*). It is insoluble in water, but soluble in alcohol, ether, and acetic acid, and is completely hydrolysed by water into dibromogallic and acetic acids. It gives a rose colour with alkalis, but no coloration with ferric chloride.

JN. W.

Oxidation Products of Isodurene. By PAUL JANNASCH and MAX WEILER (*Ber.*, 1895, **28**, 531—535; compare this vol., i, 130).—The residue left after distilling with steam the product of the oxidation of isodurene with nitric acid has now been examined. The (dibasic) acids obtained from it were converted into their methylic salts; part formed normal salts, part methyl hydrogen salts, and the latter were separated by dissolving them out with potash. Both mixtures of salts were then converted into the acids, which were subjected to sublimation; there were thus obtained, from the first portion, besides α-isodurylic acid, an *acid* melting at 334·5—335·5°, and subliming in large, hexagonal prisms, the *calcium* salt of which crystallises with $3\frac{1}{2}H_2O$; from the second portion, besides mesitylenecarboxylic acid, an *acid* melting at 297—298°, and subliming in prisms; its calcium salt crystallises with $2H_2O$. Both acids have the constitution $C_6H_2Me_2(COOH)_2$; using V. Meyer's rule for the etherification of aromatic acids, the first acid which yielded a normal methylic salt must be a *dimethylisophthalic acid* [$Me_2 : (COOH)_2 = 1:2:3:5$ or $= 1:4:2:6$], whilst the second, which yields a methyl hydrogen salt, must have the constitution [1 : 3 : 2 : 5] or [1 : 3 : 4 : 5], probably the former, since it yields no anhydride; if so it is a *dimethylterephthalic acid*.

C. F. B.

Ethereal Salts of Anhydro-α-amido-acids: Synthesis of Mercapturic acids. By FRANZ WEISS (*Zeit. physiol. Chem.*, 1895, **20**, 407—434; compare Abstr., 1893, i, 579, and 1894, i, 87).—The action of phosphorus oxychloride on phenylic hippurate (*loc. cit.*) gives rise to *phenylic anhydrohippurate*, $C_{15}H_{11}NO_2$, which melts at 42°; the *dichloro*-derivative sinters at 52°, and melts at about 150°. *Ethylic anhydrohippurate*, obtained in a similar manner from ethylic hippurate, melts at 58°; it is volatile in steam, and does not dissolve readily in water. Although indifferent towards soda, it is hydrolysed by hydrochloric acid. The *acetyl* derivative of phenylic hydroxyhippurate (*loc. cit.*) melts at 171—173°.

Phenylic anhydro-α-benzoylamidopropionate melts at 41—42°; when treated with phosphorus pentachloride, it yields *phenylic α-benzoylamido-α-chloropropionate*, which melts at 137°. Hot alkalis convert this substance into a mixture of phenol and ammonia with benzoic, hydrochloric, and probably pyruvic acids. When pentachloride of phosphorus acts on phenylic α-benzoylamidopropionate, the anhydro-compound is produced together with the foregoing substance and a nitrogenous *compound* which melts at 220—230°.

Phenylic α-bromothiophenyl-α-benzoylamidopropionate,

$$COOPh\cdot CMe(NHBz)\cdot S\cdot C_6H_4Br,$$

is obtained by acting on phenylic α-benzoylamido-α-chloropropionate with the sodium derivative of bromothiophenol in alcoholic solution; it melts at 143°, and is hydrolysed by aqueous alkalis. The *amide* crystallises in long needles, and melts at 201°.

α-Bromothiophenyl-α-benzoyllactimide, $C_6H_4Br\cdot S\cdot CMe<\begin{matrix}NBz\\ |\\ CO\end{matrix}$, is formed during the preparation of the foregoing phenylic salt. It melts at 153—155°, and is not readily hydrolysed by soda; alcoholic ammonia converts it into the amide. M. O. F.

Derivatives of Bromophenylmercapturic acids. By SIGMUND FRÄNKEL (*Zeit. physiol. Chem.*, 1895, **20**, 435—442; compare preceding abstract).—*Ethylic bromophenylmercapturate*,

$$C_6H_4Br\cdot S\cdot CMe(NHAc)\cdot COOEt,$$

melts at 91°. The *phenylic* salt is obtained by treating a mixture of phenol and mercapturic acid with phosphorus oxychloride; it melts at 96°. The *amide* melts at 174°.

The *benzoyl* derivative of bromophenylcysteïn melts at 136°; the *barium* salt crystallises from hot water, the *ethylic* salt melts at 104°, and the *phenylic* salt at 120°. This salt is not identical with phenylic bromothiophenyl-α-benzoylamidopropionate (*loc. cit.*), being geometrically isomeric with it. The *amide* melts at 191°, whilst the isomeride obtained by Weiss from inactive amidopropionic acid melts at 201°. M. O. F.

Aromatic Sulphones. By P. GENVRESSE (*Bull. Soc. Chim.*, 1894, [3], **11**, 501—514).—The *sulphone* from *phenylmethane*,

$$SO_2(C_6H_4\cdot CH_2Ph)_2,$$

prepared from the sulphone of benzylic bromide and benzene in presence of aluminium chloride, forms colourless, transparent crystals, which soon become opaque, and in air yellow. It is soluble in benzene, sparingly in hot alcohol, and melts at 162°. It is not attacked by potash.

The *sulphone of benzylidene bromide*, $SO_2(C_6H_4{\cdot}CHBr)_2$, obtained from toluenesulphonic acid and bromine at 170°, crystallises in colourless, transparent needles. It is soluble in benzene and boiling alcohol, and melts at 137°. It is oxidised by permanganate to the sulphone of benzoic acid.

The *sulphone of benzaldehyde*, $SO_2(C_6H_4{\cdot}CHO)_2 + 1\frac{1}{2}H_2O$, prepared by the action of water on the preceding compound at 170—180°, crystallises in small needles. It is soluble in benzene and alcohol, and melts at 179°. By fusion with potash it is converted into the corresponding alcohol and acid derivatives, and these are also obtained by heating the sulphone of benzylic bromide with aqueous lead nitrate. The *sodium hydrogen sulphite compound*, with $1\frac{1}{2}H_2O$, is voluminous and white; there is also an *ammonia compound*.

The *sulphone of triphenylmethane*, $SO_2(C_6H_4{\cdot}CHPh_2)_2$, obtained by the action of benzene on the sulphone of benzylidene bromide in presence of aluminium chloride, crystallises from alcohol in small, transparent crystals, which soon become opaque. It is very soluble in benzene and chloroform, and melts at 68°.

The *sulphone of triphenylcarbinol*, $SO_2(C_6H_4{\cdot}CPh_2{\cdot}OH)_2$, is formed by the oxidation of the preceding compound with chromic acid in glacial acetic acid solution. It separates from boiling alcohol in light amber coloured crystals. It is soluble in benzene and acetic acid, and melts at 78°.

The *sulphone of trinitrotriphenylmethane*,

$$SO_2[C_6H_3(NO_2){\cdot}CH(C_6H_4{\cdot}NO_2)_2]_2,$$

is a yellowish substance formed by the action of fuming nitric acid on the sulphone of triphenylmethane. It is soluble in benzene, acetic acid, and alcohol. On oxidation, it yields the corresponding *carbinol;* the yield is 60—70 per cent. of the theoretical. As precipitated by water from acetic acid solution, this is a white substance, soluble in alcohol and benzene, and melting at 100—110°.

The *sulphone of pararosaniline acetate*,

$$SO_2[C_6H_3(NH_2){\cdot}C(C_6H_4{\cdot}NH_2)_2{\cdot}OAc]_2,$$

is obtained by reducing the trinitrocarbinol with zinc dust in acetic acid solution or with tin and hydrochloric acid, and subsequent treatment with potash and acetic acid. The analytical results were not very satisfactory, probably owing to the presence of the leuco-compound. The acetate separates from acetic acid in green crystals, and, in this solvent, dyes wool, cotton, and silk without a mordant; the green colour is not very bright, but quite fast to soap and light. With potash, it forms a reddish-white precipitate, consisting probably of the free base. The *sulphone of leucopararosaniline*, $SO_2[C_6H_3(NH_2){\cdot}CH(C_6H_4{\cdot}NH_2)_2]_2$, formed by reducing trinitrotriphenylmethanesulphone with zinc dust in acetic acid solution, is a colourless, crystalline substance, soluble in alcohol.

Bi-ethylphenylsulphone, $SO_2(C_6H_4Et)_2$, is prepared from ethylbenzene and sulphuric anhydride. The yield is only 20 per cent., sulphonic acids also being formed. It is soluble in benzene and chloroform, and crystallises from alcohol in plates; the melting point is 98°, not 102°, as stated by Töhl and Eberhard (Abstr., 1894, i, 133). *Bi-isopropylphenylsulphone* is prepared in a similar manner, the yield being 16 per cent. It crystallises from alcohol in large prisms, and melts at 96°, not at 109—110°, as stated by Töhl and Eberhard. Attempts to prepare sulphones from metaxylene and mesitylene by this method failed. JN. W.

Homologues of Ethylenediphenyldisulphone and Ethylenediditolyldisulphone: Action of Halogenalkylene compounds on Mercaptides. By ROBERT OTTO (*J. pr. Chem.*, 1895, [2], **51**, 285—315; compare Abstr., 1891, 1229).—Propylenediphenyldisulphone may be prepared in the usual manner by the action of propylene dibromide on sodium benzenesulphinate, and has previously been described by Stuffer (Abstr., 1891, 180). When heated with aqueous potash, *phenylsulphonepropylic alcohol* is formed, together with potassium benzenesulphinate. The alcohol crystallises in small, white needles melting at 46°. When treated with sodium amalgam, it yields benzenesulphinic acid and normal propylic alcohol, identified by conversion into propionic acid. The *benzoate* crystallises in needles melting at 71—72°. On oxidation, the alcohol is not converted into the corresponding acid but is decomposed, benzenesulphonic acid being formed. The alcohol is accompanied by a substance which separates from ether in colourless crystals, melting at 146—147°, the constitution of which has not yet been determined.

Propylenediparatolyldisulphone, $C_7H_7{\cdot}SO_2{\cdot}CHMe{\cdot}CH_2{\cdot}SO_2{\cdot}C_7H_7$, crystallises in small plates and melts at 143—144°.

Isobutylenediphenyldisulphone could not be obtained by the action of isobutylene bromide on sodium benzenesulphinate. Isobutylene bromide, moreover, does not react with mercaptans in the presence of sodium ethoxide to form the thio-ether, but undergoes a different reaction, in which isobutylene is produced, accompanied by the sulphide corresponding with the mercaptan employed. A small quantity of the sulphone, which melts at 152°, was, however, obtained when lead phenylmercaptide was used and the thio-ether oxidised.

Pseudobutylenediphenylsulphone may be prepared from benzenesulphinic acid. It is a thick oily mass which mixes with alcohol and ether. Aqueous soda decomposes it in the normal manner, but with difficulty. Pseudobutylene bromide reacts with the mercaptans in a similar manner to isobutylene bromide in presence of sodium ethoxide. Commercial amylene bromide reacts with sodium benzenesulphinate to form a mixture of sulphones, and with both sodium and lead phenylmercaptide to form amylene and the corresponding sulphide. It was found impossible to obtain a hexylenediphenylsulphone either by the aid of benzenesulphinic acid or of a mercaptan. With dry sodium thiophenol, or the corresponding lead compound, chloracetole yields an oily substance, which is probably the thio-ether, $CMe_2(SPh)_2$. Propylidene chloride and sodium thiophenol yield the *thio-ether*,

$CH_2Me{\cdot}CH(SPh)_2$, which is an aromatic smelling oil, but has not been analysed. A. H.

Constitution of Aromatic Sulphones. By L. Zorn and H. Brunel (*Compt. rend.*, 1894, **119**, 1224—1226).—It is generally assumed that in aromatic sulphones the SO_2 group is in the para-position, but neither Genvresse (*Bull. Soc. Chim.*, [3], **9**, 513) nor Töhl and Eberhard (Abstr., 1894, i, 132, 133) have been able to obtain the sulphones of metaxylene and mesitylene, whilst Töhl and Eberhard have obtained diparaxylylsulphone by the action of sulphuryl chloride on paraxylene in presence of aluminium chloride.

In order to avoid the use of aluminium chloride, which often causes molecular transpositions, the authors have subjected well cooled paraxylene to the action of the vapours of sulphuric anhydride, care being taken that the temperature did not rise above 25°. Under these conditions diparaxylylsulphone is formed; it crystallises from alcohol in prismatic needles, melts at 141—142°, and is insoluble in water and soluble with difficulty in light petroleum, but dissolves in ether and benzene.

Under similar conditions, if the temperature is not allowed to rise above 30°, orthoxylene yields the corresponding sulphone, which crystallises from alcohol in brilliant plates melting at 158—159°. It is insoluble in water and soluble with difficulty in light petroleum, but soluble in ether and chloroform and very soluble in benzene.

The existence of the sulphones of ortho-xylene and paraxylene and the non-formation of sulphones from metaxylene and mesitylene shows that in aromatic sulphones the group SO_2 is in the meta-position. C. H. B

Action of Alkalis on Paranitrotoluenesulphonic acid. By Fritz Bender (*Ber.*, 1895, **28**, 422—425; compare O. Fischer and E. Hepp, Abstr., 1893, i, 697).—The substance obtained by the action of concentrated aqueous soda on paranitrotoluenesulphonic acid has hitherto been regarded as the sodium salt of dinitrosostilbenedisulphonic acid (*loc. cit.*); it consists, however, of a mixture of two compounds which the authors have identified as the salts of *dinitrodibenzyldisulphonic acid* and *azoxystilbenedisulphonic acid;* the latter dissolves in concentrated sulphuric acid with development of a red coloration; its *barium* salt is very slightly soluble. When reduced with stannous chloride and hydrochloric acid, azoxystilbenedisulphonic acid yields diamidostilbenedisulphonic acid, and oxidation with potassium dichromate and sulphuric acid converts it into dinitrostilbenedisulphonic acid.

Dinitrodibenzyldisulphonic acid is an intermediate product, the further action of alkali converting it into a stilbene derivative. The solution in concentrated sulphuric acid is orange-coloured; on reduction, it yields diamidostilbenedisulphonic acid. M. O. F.

Action of Carbonyl Chloride on Derivatives of Sulphonic and Sulphinic acids. By P. Tischendorf (*J. pr. Chem.*, 1895, [2], **51**, 350—352).—Carbonyl chloride reacts with phenylsulphonephenylamide in the normal manner, *diphenylsulphonediphenylcarbamide*,

$CO(NPh\cdot SO_2Ph)_2$, which melts at 198°, being formed. Paratolylsulphonephenylamide reacts in a similar manner, *diparatolylsulphonediphenylcarbamide*, melting at 210°, being produced. On the other hand, phenylsulphonamide yields a substance melting at 155° of which the constitution has not yet been determined, and an analogous product, melting at 180°, is obtained from paratolylsulphonamide. These two compounds seem to be formed from three molecules of the original sulphonamide and are acids, whilst the normal derivatives are indifferent substances.

Sodium benzenesulphinate does not yield any analogous compound with phosgene. A. H.

The Red Isomeride of Indigotin. Some Derivatives of Isatin. By Edward Schunck and Leo Marchlewski (*Ber.*, 1895, **28**, 539—547).—Naturally occurring indirubin, "indigopurpurin" obtained by the reduction of isatin chloride (Baeyer, Abstr., 1879, 535), and synthetical indirubin obtained from isatin and indoxyl (Abstr., 1882, 199), have been compared and found to be identical; the most probable formula for the substance is $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C{:}C<\begin{matrix}CO\\C_6H_4\end{matrix}>NH$.

Isatin phenylhydrazone yields an *acetyl derivative*,

$$C_6H_4<\begin{matrix}C(N_2HPh)\\\text{———}\\N\end{matrix}>C\cdot OAc,$$

which forms yellow crystals, and melts at 131° when heated quickly. Isatin also yields a 1 : 4-*tolylhydrazone*, crystallising in yellow needles melting at 233°, and 1 : 2-*tolylhydrazone*, which forms yellow needles melting at 240—241°; the latter yields an *acetyl* derivative crystallising in yellow needles and melting at 167°. Metachlorisatin yields a 1 : 4- and a 1 : 2-*tolylhydrazone*, and a *β-oxime*, which crystallise in yellow needles and melt respectively at 253°, 273—274°, and 252°. Bromisatin yields a yellow, crystalline *phenylhydrazone*, melting at 271—272°, the yellow *acetyl* derivative of which melts at 224°. Nitroisatin yields a yellow acetyl derivative, *acetylpseudonitroisatin*, which melts at 193—194°, and from which, when it is dissolved in cold aqueous alkali and the solution acidified with acetic acid, the yellow *acetylnitroisatic acid*, $NO_2\cdot C_6H_3(NHAc)\cdot CO\cdot COOH$, is obtained; this yields nitroisatin when it is boiled with acids. Nitroisatin further yields a *phenylhydrazone* and a 1 : 4- and a 1 : 2-*tolylhydrazone*; these are dark yellow, and melt at 284°, 274—275°, and above 290° respectively.

C. F. B.

Metadichlor- and Metadibrom-indigo. By Adolf Baeyer and Ernst Wirth (*Annalen*, 1895, **284**, 154—157; compare this vol., i, 282).—3 : 6-*Bromonitrostyryl methyl ketone*,

$$NO_2\cdot C_6H_3Br\cdot CH{:}CH\cdot COMe,$$

forms yellowish needles which melt at 165·5—166°; it is prepared by the action of boiling acetic anhydride on bromonitrophenylhydroxyethyl methyl ketone. When the latter is treated with caustic soda the

solution becomes yellow and a precipitate of metadibromindigo is formed. This colouring matter closely resembles indigo; the vapour is reddish-violet. It dissolves in hot aniline and in chloroform, but it is almost insoluble in melted paraffin. When treated with concentrated sulphuric acid, it undergoes sulphonation; dibromindigo is decolorised by alcoholic potash and undergoes oxidation with nitric acid.

Dichlorindigo resembles the dibromo-derivative; it is prepared in a similar manner from 3 : 6-chloronitrophenylhydroxyethyl methyl ketone. M. O. F.

Conversion of Isodiazohydroxides into Derivatives of Diphenyl. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 403—407; compare Kühling, this vol., i, 182).—By allowing paranitroisodiazobenzene hydroxide to remain in benzene, or its sodium salt in benzene and acetic acid, or its methylic salt in boiling benzene, paranitrodiphenyl is obtained; $NO_2 \cdot C_6H_4 \cdot N_2 \cdot OH + C_6H_6 \rightarrow NO_2 \cdot C_6H_4 \cdot C_6H_5$. In a similar manner, the other compounds mentioned below were prepared; the numbers given are melting points.

Diphenyl. Parabromodiphenyl, lustrous, white plates, with odour of oranges, 90°. *Paranitrodiphenyl*, very pale yellow needles, 114—114·5°. *Orthomethylparanitrodiphenyl*, colourless, glassy needles, 56—57°. *Paranitrophenyltolyl*, lustrous, white needles, 104°; reduced by tin and hydrochloric acid to *paramidophenyltolyl*, the *acetic derivative* of which melts at 147°. C. F. B.

Syntheses with Sodamide Derivatives. By CARL BLACHER (*Ber.*, 1895, **28**, 432—437).—The *sodium* compound of acetamide, of benzamide, or of phenylcarbamide is obtained from a mixture of sodium ethoxide and the amide (1 mol.) in alcoholic solution on removing the solvent by distillation under reduced pressure.

Benzoylbenzylamine is formed when sodium benzamide, suspended in xylene, is heated for 13 hours with benzylic chloride in a reflux apparatus fitted with a tube of calcium chloride. Under similar conditions benzoic chloride and sodium benzamide give rise to a mixture of di- and tri-benzamide.

When a solution of iodine (1 mol.) in xylene is added to boiling xylene in which sodium benzamide is suspended, it is immediately decolorised, with formation of benzoylphenylcarbamide, which melts at 204—205°. If benzene or toluene is employed as the medium, an isomeric *compound*, $C_{14}H_{12}N_2O_2$, is formed; this melts at 180—185°.

Synthetical products were not obtained by the action of sodium benzamide on ethylic chloracetate or chloroformate, the salts undergoing decomposition prior to the formation of sodium chloride. M. O. F.

Action of Acid Chlorides on Methyl Paraisobutylphenyl Ether. By FRANK B. DAINS (*Amer. Chem. J.*, 1895, **17**, 114—116).—By the action of acetic chloride, *orthomethoxymetisobutylacetophenone*, $OMe \cdot C_6H_3Bu^{\beta} \cdot COMe$, is formed. It is an oil which boils at 262—265° under 749 mm. pressure, and does not solidify at −18°. With

hydroxylamine, it yields a *ketoxime* crystallising in needles melting at 113—114°.

With benzoic chloride, *orthomethoxyparaisobutylbenzophenone* is formed, boiling above 315°. L. T. T.

Displacement of Isodiazo-groups by Cyclic Radicles. By Otto Kühling (*Ber.*, 1895, **28**, 523—527; compare this vol., i, 182).—The following compounds were prepared from anhydrous finely-divided sodium paranitrophenylnitrosamine in presence of acetic chloride or glacial acetic acid; the yield in most cases was poor. The constitution of the compounds is not definitely proved, but the substituting groups are probably in the para positions 4, 4'.

Paranitrophenylbenzaldehyde, $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot CHO$, obtained from benzaldehyde and the sodium nitrosamine, crystallises in minute plates, melts at 115—120°, and yields a crystalline *hydrogen sodium sulphite* derivative. *Paranitrophenylacetophenone*, $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot COMe$, formed from the nitrosamine and acetophenone, crystallises in slender, pale yellow needles, and melts at 90—94°. No oxime could be obtained. *Paranitrophenylbenzoic acid*, $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot COOH$, is prepared from ethylic benzoate and the nitrosamine, the resulting uncrystallisable *ethylic salt* being hydrolysed with alcoholic potash; it is a crystalline, yellowish powder, melts at 189°, and when slowly heated evolves carbonic anhydride at 100°. It dissolves in alkalis and alkali carbonates with a yellow colour. *Paranitrohydroxydiphenyl*, $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot OH$, is obtained from ethoxybenzene and the nitrosamine; the *ethylic salt* which is first formed does not crystallise; the phenol is deposited in slender, yellow needles, melts at 120°, and gives a reddish-brown coloration with ferric chloride. Schmidt and Schultz give the melting point of 4 : 4'-nitrohydroxydiphenyl as 170°. *Paranitrophenylbenzylic alcohol*, $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_2 \cdot OH$, formed from benzylic alcohol and the nitrosamine, crystallises in slender, colourless, concentrically-grouped needles, and melts at 121—122°.

Paranitrophenylpyridine, $NO_2 \cdot C_6H_4 \cdot C_5NH_4$, prepared from pyridine and the nitrosamine, crystallises in aggregates of small yellow needles, and melts at 117°, with previous softening at 109°. It is a feeble base, and dissolves in dilute acids; the *hydrochloride* is unstable, the *sulphate* stable. In reply to Bamberger's criticism (*Ber.*, **28**, 403) of his previous paper (*loc. cit.*), the author repeats his conviction that the sodium salt acts in the tautomeric form, $NO_2 \cdot C_6H_4 \cdot N{:}NONa$, and that acidyl derivatives are produced by its interaction with acid chlorides in presence of anhydrous benzene. Support for this view is found in the readiness with which the nitrogen is eliminated.

J. B. T.

Diphenylorthophthalide. By Bronislaw Pawlewski (*Ber.*, 1895, **28**, 513—514).—*Diphenylorthophthalide*, $CO<\begin{matrix}C_6H_4\\O\end{matrix}>C(C_{12}H_9)_2$, is prepared by Friedel-Craft's method from diphenyl and phthalic chloride; it is purified with difficulty, crystallises from acetic acid in granules or small plates, softens at 98—100°, and is not completely melted at 120°. When warmed with concentrated sulphuric acid, a cherry-red coloration is formed, which slowly changes to dull green;

at ordinary temperatures, the colour produced is deep blue, changing somewhat quickly to violet. The yield is 30 per cent. of the theoretical. Variation in the proportion of diphenyl employed is without effect on the composition of the resulting product. J. B. T.

Fluoresceïn Ethers. By Otto Fischer and Eduard Hepp (*Ber.*, 1895, **28**, 396—399; compare Nietzki and Schröter, this vol., i, 183).—When fluoresceïn is boiled with caustic potash and methylic iodide in methyl alcoholic solution, it yields a *dimethyl compound*,

$$COOMe\cdot C_6H_4\cdot C<\begin{matrix}C_6H_3(OMe)\\C_6H_3(:O)—\end{matrix}>O,$$

which forms orange, or deep red, metallic crystals, melts at 208°, and gives a green fluorescence in alcoholic solution; none of the colourless isomeride, which melts at 198° (this vol., i, 55), is formed. This dimethyl compound is converted by dilute sodium hydroxide into a nearly colourless *monomethyl ether*,

$$COOH\cdot C_6H_4\cdot C<\begin{matrix}C_6H_3(OMe)\\C_6H_3(:O)—\end{matrix}>O,$$

which melts at 262°, gives a yellow coloration with green fluorescence in alkaline solution, and, when boiled with aniline and aniline hydrochloride, yields an *anilide*, $NPh:C<\begin{matrix}C_6H_4\\—O—\end{matrix}>C<\begin{matrix}C_6H_3\cdot OMe\\C_6H_3\cdot OH\end{matrix}$, which forms colourless crystals, and gives no colour or fluorescence in alkaline solution, although in strong sulphuric or hydrochloric acid solution it is yellow with green fluorescence. The property of fluorescence in alkaline solution seems to depend, in the case of the anilides, on one particular hydroxyl group remaining intact, namely, that which is still present in the compounds with a quinonoid formula, and which in the anilide of the monomethyl ether is replaced by methoxyl. C. F. B.

Constitution of Fluoresceïn. By Richard Meyer (*Ber.*, 1895, **28**, 428—432; compare Abstr., 1892, 1228).—When fluoran is gently heated with fused caustic alkali, a mixture of benzoic and salicylic acids with orthodihydrobenzophenone and phenol is formed.

The salts of hydrofluoranic acid (*loc. cit.*) are characterised by a low degree of solubility; the *sodium* salt forms colourless plates which resemble naphthalene. The *barium* and *magnesium* salts form minute crystals, whilst the *strontium*, *zinc*, *copper*, and *silver* salts are amorphous. The *methylic* salt crystallises in long needles, and melts at 123—125°; the *ethylic* salt separates from alcohol in plates and melts at 99—101°. M. O. F.

Oxidation of Naphthalene Tetrachloride. By D. Helbig (*Ber.*, 1895, **28**, 505—507).—Naphthalene tetrachloride, $C_{10}H_8Cl_4$ [$Cl_4 = 1:2:3:4$], when oxidised with nitric acid (sp. gr. 1·45), yields dichloronaphthaquinone [$CO = 1:4$; $Cl_2 = 2:3$] which melts at 196°, not 189° as stated by Graebe. With chromic anhydride in glacial acetic acid solution, naphthalene tetrachloride gives 3 : 4-

dichloro-1-naphthol; when this is exposed to the air in alkaline solution, a deep blue compound is formed which is being further investigated. The oxidation of naphthalene tetrachloride with potassium permanganate has not led to any definite results. J. B. T.

New Formation of Secondary Amines. By Otto Kym (*J. pr. Chem.*, 1895, [2], **51**, 325—335).—α-Bromonaphthalene reacts with aniline and paratoluidine in the presence of soda-lime in the same way as bromobenzene (Merz and Paschkowezky, Abstr., 1894, i, 122). The product, however, consists not of the corresponding derivative of α-naphthylamine, but the isomeric β-compound. Molecular change, therefore, takes place in this reaction, and the same thing is observed when α-chloronaphthalene is heated with paratoluidine and soda-lime, paratolyl-β-naphthylamine being formed. A somewhat similar change occurs when paradibromobenzene is heated with paratoluidine and soda-lime, diparatolylmetaphenylenediamine being produced, and not the expected derivative of paraphenylenediamine. A. H.

Chrysophanic acid. By Oswald Hesse (*Annalen*, 1895, **284**, 191—195).—Chrysophanic acid has been the subject of much investigation. It is isolated from the root of the rhubarb plant by extracting it several times with ether; the accumulated extracts, with exception of the first, are evaporated, and the residue is treated with a small quantity of alcohol, filtered, and dissolved in chloroform. On removing the solvent by evaporation and treating the residue with warm aqueous potassium carbonate, the substance remains undissolved. Chrysophanic acid crystallises from alcohol in small leaflets and melts at 178°; the analysis of the compound agrees with the formula $C_{15}H_{10}O_4$. Hydriodic acid converts it into chrysophanohydroanthrone, $C_{15}H_{12}O_3$, which melts at 196° (Abstr., 1888, 492).

M. O. F.

Picene. By Eugen Bamberger and Frederick D. Chattaway (*Annalen*, 1895, **284**, 52—80; compare Abstr., 1893, i, 594).—On distilling picenequinone with zinc dust, picene is obtained in nacreous plates which exhibit a blue fluorescence. When the vapour of the hydrocarbon is led through a red-hot tube containing hydrogen, hydropicene, $C_{22}H_{28}$, is formed; it is also obtained by the action of heated litharge on picenequinone. Hydropicene forms small needles and melts at 285°; distillation with zinc dust converts it into picene.

Picenequinone or *picylenediketone*, $\begin{matrix} C_{10}H_6{\cdot}CO \\ | \\ C_{10}H_6{\cdot}CO \end{matrix}$, is produced when picene, suspended in boiling glacial acetic acid, is treated with a solution of chromic anhydride in the same solvent; a small quantity of picenequinonecarboxylic acid is formed at the same time. The quinone is a brick-red, crystalline powder which yields lustrous, red leaflets and needles on sublimation; when distilled with soda lime, it gives rise to ββ-dinaphthyl and picene.

Picylene ketone, $C_{20}H_{12}{:}CO$, may be prepared in several ways. It is formed when a mixture of picenequinone or picenequinonecarboxylic acid and litharge is distilled in a vacuum; the ketone is obtained by distilling picenic acid from lime, and by heating the silver salt at

150—200°; it is also prepared from picenic acid by the action of cold concentrated sulphuric acid. Picylene ketone is a golden-yellow powder which melts at 185·5°; it dissolves in concentrated sulphuric acid with development of a violet coloration, and is precipitated from the solution on the addition of water.

Picylenecarbinol, or *picenefluorene alcohol*, $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!>\!CH\cdot OH$, is prepared by reducing the foregoing ketone with zinc dust and hydrochloric acid; sodium amalgam may also be employed as the reducing agent. It melts at 230° and dissolves in warm concentrated sulphuric acid with development of a blue coloration. The *acetyl*-derivative crystallises in slender, white needles and melts at 159°.

Picylenemethane, or *picenefluorene*, $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!>\!CH_2$, is formed when picylene ketone is heated with hydriodic acid and phosphorus for four hours at 170—175°; it melts at 306°, and the solution in concentrated sulphuric acid is green.

Picenic ($\beta\beta$-dinaphthylcarboxylic) acid, $C_{10}H_7\cdot C_{10}H_6\cdot COOH$, is prepared by acting on picylene ketone with fused potash. Picenequinone also yields the acid under this treatment, but in much smaller quantity, picylene ketone, picene, hydropicene, and dinaphthyl being formed at the same time. Picenic acid melts at 201°; the *barium*, *calcium*, and *silver* salts are colourless, and are not readily soluble in water.

It has already been stated (*loc. cit.*) that picenic acid when distilled from lime in a vacuum yields $\beta\beta$-dinaphthyl. If the operation is carried out under atmospheric pressure, a *hydrocarbon*, which melts at 235°, is formed; it crystallises from alcohol in white, nacreous plates.

Picenequinonecarboxylic acid, $\begin{matrix}COOH\cdot C_{10}H_5\cdot CO\\C_{10}H_6\cdot CO\end{matrix}$, is obtained by the oxidation of picene with potassium dichromate and sulphuric acid; it is a red, crystalline powder which becomes black at 250° and decomposes at about 330°. The solution in concentrated sulphuric acid is dark violet, whilst alkalis and alkali carbonates dissolve it with development of a deep red coloration. The *silver* salt is a dark red powder; when heated in small quantities at 180—200°, it yields a sublimate of picenequinone. On distilling picenequinonecarboxylic acid from lime, picene is produced, and the hydrocarbon is also formed, together with hydropicene and picylene ketone, when picenequinonecarboxylic acid is distilled from litharge in a vacuum. In preparing picenequinonecarboxylic acid by oxidation of picene, phthalic acid is formed in small quantity; this substance is also produced on oxidising picenequinonecarboxylic acid with potassium permanganate.

Picenecarboxylic acid, $\begin{matrix}COOH\cdot C_{10}H_5\cdot CH\\C_{10}H_6\cdot CH\end{matrix}$, is prepared by heating picenequinonecarboxylic acid with hydriodic acid and phosphorus for eight hours at 170—180°; it is a white powder which melts at 245°. The *silver*, *barium*, and *calcium* salts do not dissolve in water. When the acid is distilled from lime in a vacuum, picene is formed.

M. O. F.

Pine Tar. By ADOLPHE RENARD (*Compt. rend.*, 1894, **119**, 1276—1277).—The products of the distillation of pine tar boiling above 300° consist of a mixture of diterebenthyl, $C_{20}H_{30}$, boiling at 332—338°, and diterebenthylene, $C_{20}H_{28}$, boiling at 340—345°, identical with those found in resin oils, except that in the latter the diterebenthyl is present in much higher proportion. The two are readily separated by the action of sulphuric acid, which converts diterebenthyl into a sulphonic derivative, but has no action on diterebenthylene. Didecene, which is found in resin oils, is not present in the products of the distillation of pine tar. The final fractions contain retene, which is readily purified by pressure and crystallisation from alcohol.

The phenols obtained by the action of sodium hydroxide on the crude product of distillation of the tar, boil almost entirely between 190° and 230°, 66 per cent. boiling between 200° and 220°. The fraction 200—210°, when analysed by Béhal and Choay's method, was found to consist of monhydric phenols, 40·0 per cent.; guaiacol, 20·3 per cent.; creosol and its homologues, 37·5 per cent. The fraction 210—220° contained no guaiacol. So far as regards the proportion of guaiacol, pine-tar creosote is intermediate between that from the beech and that from the oak (compare Abstr., 1894, i, 612).

C. H. B.

Rotatory Power of Oil of Spike and Oil of Lavender. By GUSTAVE MASSOL (*J. Pharm.*, 1895, [6], **1**, 49—50).—The author has determined the rotation of samples of known origin and purity. He found for oil of lavender, $[\alpha]_D = -3·70°$, and sp. gr. = 0·930 at 15°; and for oil of spike, $[\alpha]_D = +9·66°$, and sp. gr. = 0·935 at 15°. Buignet found, for lavender, $[\alpha]_D = -21·20°$, and sp. gr. = 0·886; for spike, $[\alpha]_D = +3·30°$, sp. gr. = 0·886; and Bruylants, for lavender, $[\alpha] = -4·01°$, and sp. gr. = 0·876; and spike, $[\alpha] = -0·64°$, and sp. gr. = 0·908. It is thus clear that the rotatory power and density of these oils are dependent on the character of the season, soil, &c., and cannot be used as tests of purity.

L. T. T.

Essence of Ylang-ylang. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1894, [3], **11**, 577—583).—The sesquiterpene mentioned in the previous paper (this vol., i, 243) consisted mainly of a fraction boiling at 138·5—143°. The sp. gr. = 0·91 at 15°, the refractive index = 1·50001 at 20°, the rotatory power of the liquid = +46·4° for 20 mm.; of the alcoholic solution (about 9 per cent.), $[\alpha]_D = +6·8°$. The molecular refraction is 66·32, a number pointing to the presence of two ethylene bands in the molecule. The *hydrochloride*, $C_{15}H_{24}$,2HCl, crystallises from ethylic acetate in brilliant needles and melts at 117°. A small quantity of a solid polyterpene was also isolated.

On repeating the work on a fresh portion of essence, a considerable quantity of acetic acid was found in alcoholic combination. The constants of the ylangol obtained were as follows, at 17°:—sp. gr. = 0·8907; refractive index = 1·4747; molecular refraction = 48·64; specific rotatory power in alcoholic solution, $[\alpha]_D = -19·3°$. A small quantity of the *sodium hydrogen sulphite compound* of the oxidation product of the ylangol was isolated.

The proximate percentage composition of essence of ylang-ylang is

thus:—benzoic acid, 9; acetic acid, 7; ylangol, 30—32; sesquiterpene, 30; polyterpenes and volatile products, 20. Jn. W.

Metallic Campholates. By Guerbet (*Bull. Soc. Chim.*, 1894, [3], **11**, 486—491).—A revision and completion of Kachler's and Malin's work (*Annalen*, 1872, **162**, 259, and 1868, **145**, 201).

Ammonium campholate, $C_{10}H_{17}O_2NH_4$, is prepared by the action of dry ammonia on an ethereal solution of campholic acid; it is very unstable, and dissociates rapidly in air, and at once in water, so that Kachler's statement that it can be obtained by evaporating an ammoniacal solution of the acid is not correct; the acid itself remains. The *potassium*, with $2H_2O$; *sodium*, with $5H_2O$; *barium*, with $3H_2O$; *strontium*, *calcium*, *magnesium*, *zinc*, *copper*, *nickel*, and *cobalt* salts were prepared and analysed. Jn. W.

Alkylic Campholates. By Guerbet (*Bull. Soc. Chim.*, 1894, [3], **11**, 491—496).—The alkylic campholates can be prepared by the action of campholic chloride on the respective alcohols. The yield obtained by the action of the free acid on the alcohols is very poor; the rate of formation of the isobutylic salt, for instance, is never greater than 0·1, and the limit of etherification at 155—170° is 27·1 per cent. The acid properties of campholic acid are thus extremely feeble, and the alkylic salts resemble ethers rather than ethereal salts; they are not hydrolysed by aqueous or alcoholic alkalis under ordinary conditions, but are readily decomposed by hydrogen chloride or iodide; they are completely hydrolysed, however, by alcoholic sodium ethoxide at 150°.

The alkylic campholates are colourless, oily liquids of agreeable odour. *Methylic campholate*, $C_{10}H_{17}O_2Me$, boils at 208°, and has sp. gr. = 0·9723 at 0°. The *ethylic* salt boils at 220° (750 mm.) and at 106—107° (20 mm.), and has sp. gr. = 0·9534 at 0°; it does not solidify at −20°; the odour resembles that of peppermint. The *isopropylic* salt boils at 228°, and has sp. gr. = 0·9377 at 0°. The *isobutylic* salt boils at 250°, and has sp. gr. = 0·9365 at 0°. The *amylic* salt boils at 263—265°, and has sp. gr. = 0·9361. The *phenylic* salt melts at 22° and boils at 305°; the odour recalls that of phenol. Jn. W.

Camphoric acid. By William A. Noyes (*Ber.*, 1895, **28**, 547—555).—A preliminary notice; the full account will appear in the *Amer. Chem. J.*—Dihydroamidocampholytic acid (Abstr., 1894, i, 339), when treated with nitrous acid, yields *dihydrohydroxycampholytic acid*, $OH{\cdot}C_8H_{14}{\cdot}COOH$, melting at 132°; this is probably a β-hydroxy-compound, and, if so, camphoric acid has its two carboxyl groups attached to neighbouring carbon atoms.

Liquid (cistrans) campholytic acid, when warmed with dilute sulphuric acid, is transformed into an isomeric *iso-* or *cis-campholytic acid*, melting at 133·5°, identical with the camphothetic acid of Walker (Trans., 1893, 504) and the isolauronolic acid of Kœnigs and Hœrlin (Abstr., 1893, i, 363); the author regards the two acids as stereoisomeric, containing respectively, in the group –CMe:C(COOH)–,

the Me and COOH on opposite and on the same side of the plane of the ring. The cistrans acid yields a *hydrobromide* melting at 98—100°, and a *dibromide* melting at 114°; the cis-acid, although with difficulty, a *hydrobromide* melting at 127—130°, and a *dibromide* melting at 138—140°.

Amidolauronic acid was treated with nitrous acid, and the following products were isolated. (1) A *hydrocarbon*, C_8H_{14}, boiling at 122°, and with sp. gr. = 0·8033 at 15°/15°, = 0·8004 at 20°/20°, probably identical with the one obtained by Aschan (this vol., i, 154). (2) Unsaturated ($\beta\gamma$) *isolauronolic acid*, $C_8H_{13}\cdot COOH$; its *calcium salt* crystallises with $2H_2O$; the *amide* is liquid; heating with dilute sulphuric acid converts the acid into campholactone. (3) *Isocampholactone*, melting at 23°, probably stereoisomeric with campholactone. (4) An *acid* melting at 180°, perhaps

$$COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CMe(COOH)_2.$$

C. F. B.

Camphoric Dianilide. By Ossian Aschan (*Ber.*, 1895, **28**, 530—531).—Camphoric chloride is mixed with rather more than 2 mols. of aniline, both substances being dissolved in ether and the mixture kept cool; aniline hydrochloride is then removed by shaking with water, and the ethereal solution allowed to remain; crystals of the *dianilide*, $C_8H_{14}(CO\cdot NHPh)_2$, are deposited. The dianilides from *d*- and *l*-camphoric acid are entirely similar in properties, and melt at 226°; those of the optically isomeric isocamphoric acids also resemble each other, but they melt at 201°, and are much more soluble in alcohol and acetic acid than the two first mentioned. C. F. B.

Chlorophyll. By Edward Schunck and Leo Marchlewski (*Annalen*, 1895, **284**, 81—107; compare Abstr., 1893, i, 41, and 1894, i, 341).—Alkachlorophyll is prepared by a method differing only in minor particulars from the process already described (*loc. cit.*). The product undergoes no apparent change on dissolution in hydrochloric acid, and the colour of the liquid remains unaltered for many days; on pouring the solution into water, however, ether extracts phyllotaonin, and ethylphyllotaonin is formed when the solution in hydrochloric acid is poured into boiling alcohol, a purple-blue coloration being developed. Concordant analyses of alkachlorophyll agree equally well with the formulæ $C_{30}H_{34}N_4O_4$ and $C_{52}H_{37}N_7O_7$, but its behaviour, when treated with hydrochloric acid, points to the latter expression as representing the composition, because phyllotaonin has already been shown to have the formula $C_{40}H_{40}N_6O_6$.

Alkachlorophyll is a dark, greenish-blue substance, which dissolves readily in alkalis, forming dark, emerald-green solutions, exhibiting a strong, red fluorescence. The sodium salt resembles it in appearance, and the absorption spectrum of the aqueous solution differs but slightly from that of the colouring matter itself. When alkachlorophyll is heated for several hours at 190—200° with alcoholic potash, brownish-red crystals are obtained, which dissolve in hydrochloric acid, forming a reddish-violet solution; on neutralising the filtered liquid with soda and acidifying with acetic acid, ether extracts a

substance which the authors term *phylloporphyrin;* it is not identical with the compound to which this name has been applied by Hoppe-Seyler, who obtained it from dichromatic acid by the action of acids. The spectrum of an ethereal solution of alkachlorophyll shows, in addition to the four absorption bands of chlorophyll, a fifth band at F, but this does not appear when hydrochloric acid is the solvent employed.

Phylloporphyrin is prepared by heating phyllotaonin for several hours at 190° with alcoholic potash; on diluting the liquid and acidifying with hydrochloric acid, ether extracts a brown substance. This is boiled with alcohol, filtered, and the filtrate treated with an alcoholic solution of zinc acetate. The red, crystalline substance slowly deposited from this solution is a zinc salt, which is decomposed by adding hydrochloric acid to the hot alcoholic solution, this being then poured into a large quantity of water and extracted with ether. Evaporation of the solvent yields phylloporphyrin, which, on recrystallisation from alcohol, is obtained in short, reddish-violet prisms. Analysis gives results which agree with the formula $C_{32}H_{34}N_4O_2$. Phylloporphyrin is easily soluble in chloroform, but dissolves with difficulty in alcohol, ether, and carbon bisulphide, giving red solutions, which exhibit fluorescence of the same colour; this acquires a bluish tint on the addition of acids. Phylloporphyrin has basic properties, but it also forms metallic salts. The spectrum of an ethereal solution has seven absorption bands; a plate representing the spectra of solutions in sulphuric and hydrochloric acids and in ether, together with the aqueous solution of the zinc salt, appears in the original paper, which also contains a detailed description of the method by which the authors have succeeded in converting phylloxanthin into phyllocyanin. M. O. F.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1895, **284**, 107—132).—*Pinastric acid*, $C_{10}H_8O_3$, is the pigment to which *Cetraria pinastri* (Scopoli) owes its yellow colour; the air-dried lichen is extracted with ether, and the residue obtained on evaporating the solvent is recrystallised several times from absolute alcohol in order to remove the usnic acid which is present. Pinastric acid crystallises from alcohol in golden-yellow prisms, and melts at 203—205°. Alkalis and alkali carbonates dissolve it, forming yellow solutions which are decomposed by carbonic anhydride; the solution in concentrated sulphuric acid is yellow. When heated for an hour with acetic anhydride, pinastric acid is converted into a *compound*, $C_{19}H_{16}O_6$, crystallising from alcohol in lustrous, greenish needles which melt at 171—173°. Pinastric acid has toxic properties; it occurs in several other yellow lichens.

Soloric acid, $C_{15}H_{14}O_5$, is the substance giving rise to the red colour which characterises the under surface of the thallus of *Solorina crocea* (L.). On extracting the lichen with chloroform, and evaporating the dark, reddish-brown liquid, a crystalline mass is obtained which, after being recrystallised several times from benzene and a mixture of benzene and alcohol, yields small, red, lustrous crystals which melt at 199—201°; these crystals are pleochroïc. Reddish-

yellow or reddish-brown solutions are formed by dissolving soloric acid in chloroform, benzene, light petroleum, ether, and alcohol; it is insoluble in water. Soda and potash form violet solutions, whilst, if warmed with ammonia or alkali carbonates, it gives purple-violet solutions which are decomposed by carbonic anhydride. Crystals of the acid, when treated with boiling aqueous barium hydroxide, become dark violet, but remain undissolved; it is insoluble in nitric acid, and dissolves without change in concentrated sulphuric acid, being reprecipitated from the purple solution on diluting it with water. Boiling acetic anhydride converts soloric acid into a *diacetyl* derivative which crystallises in small, golden-yellow needles, and melts at 147—148°.

Rhizocarpic acid, $C_{13}H_{10}O_3$, is obtained from *Rhizocarpon geographicum* (L.) and *R. lecanorinum* by extraction with chloroform and recrystallisation of the product from absolute alcohol; it crystallises in lemon-yellow, rhombic prisms, and melts at 177—179°. Alkalis and alkali carbonates dissolve the acid forming yellow or yellowish-green solutions which are not decomposed by carbonic anhydride; it is soluble in concentrated sulphuric and nitric acids. When treated with boiling acetic anhydride, rhizocarpic acid is converted into ethylpulvic acid which melts at 128°. Rhizocarpic acid also occurs in *Pleopsidium chlorophanum* (Wahlenberg), *Raphiospora flavorirescens* (Borr.), and *Biatora lucida* (Ach.). From the first-named of these, a compound was also obtained which melts at 144—145°; it crystallises in colourless, silvery leaflets belonging to the tetragonal system, and, from its source, the author terms it *pleopsidic acid*.

Methylic hydrogen pulvate or vulpic acid (J. Volhard, this vol., i, 99) occurs in the lichens *Calycium chlorinum* (Korber), *C. c.* (Stenh.), and *Cyphelium chrysocephalum* (Ach.), whilst *Callopisma vitellinum* (Ehrhardt), and *Physcia medians* (Nylander) contain the ethylic salt.

Calycin (Hesse, Abstr., 1881, 180) is present in the lichens *Lepra candelaris* (Schaerer), *L. chlorina* (Ach.), *Calycium Stenhammari*, *Callopisma vitellinum* (Ehrhardt), *Gyalolechia aurella* (Hoffm.), *Physcia medians* (Nylander), and *Candelaria concolor* (Dicks). On agitating a solution of calycin in chloroform or benzene with aqueous soda or potash, a brick-red substance is produced; this is taken up by the alkali, leaving the organic solvent colourless. The lichen from which calycin was first isolated is *Lepra candelaris* (compare *loc. cit.*); vulpic acid occurs in *Calycium* (*cyphelium*) *chrysocephalum*; but this lichen does not contain calycin.

Psoromic acid (Spica, Abstr., 1883, 80) occurs in *Rhizocarpon geographicum* (L.), together with rhizocarpic acid. The author has obtained zeorin from *Physcia cæsia* (Hoffmann), and *P. endococcina*.

M. O. F.

Compounds from Lichens. By Oswald Hesse (*Annalen*, 1895, **284**, 157—191).—Usnic acid, $C_{18}H_{16}O_7$, is obtained from *Usnea barbata var. ceratina*; it melts at 195—196°. An intense brownish-red coloration is developed in the alcoholic solution by ferric chloride. When heated with acetic anhydride at 85°, the *anhydride*, $C_{36}H_{30}O_{13}$, is formed; it crystallises in lustrous, yellow needles, and melts at 189°. The potassium salt contains $3H_2O$, the sodium and lead salts,

$2H_2O$, and the barium and calcium salts, $4H_2O$; the copper and silver salts are anhydrous. When usnic acid is heated at 120° with phenylhydrazine, a *dihydrazone*, $C_{30}H_{28}N_4O_5$, is formed. It separates from alcohol in large crystals containing $3H_2O$, and melts at 229°.

On heating usnic acid for four hours with alcohol at 150°, decarbusneïn, $C_{17}H_{16}O_6$, is formed (compare Paternò, Abstr., 1882, 1080). It crystallises in small, white needles, and melts at 175°; treatment of the alcoholic solution with ferric chloride gives rise to a reddish-brown coloration. The acetyl derivative is obtained by the action of acetic anhydride at 85° (compare *loc. cit.*); it melts at 112°, and the alcoholic solution gives a violet coloration with ferric chloride. The action of 50 per cent. potash at 100° converts usnic acid into resinous products together with acetone and carbonic anhydride. When treated with concentrated sulphuric acid, usnic acid yields the isomeric usnolic acid (Stenhouse and Groves, Trans., 1881, 235); this melts at 206—208°, gas being evolved at 210°.

Barbatin, $C_9H_{14}O$, is obtained from the same source as usnic acid. It crystallises from glacial acetic acid in colourless needles, and melts at 209°; it may be distilled without undergoing change. Carbon-usnic acid occurs in the lichens *Usnea barbata var. florida* and *hirta*. *Parmelia perlata* contains vulpic and usnic acids; a compound, $C_{16}H_{16}O_7$, which the author terms *parmelin*, is also present; it melts at 187°, and is soluble in aqueous alkalis.

Coccellic acid, $C_{20}H_{22}O_7$, is obtained from *Cladonia coccifera*; it crystallises from glacial acetic acid in colourless prisms, and melts and evolves gas at 178°, forming a white sublimate. Ferric chloride colours the alcoholic solution bluish-violet, whilst calcium hypochlorite develops an intense yellow colour which is destroyed on further addition of the reagent. When coccellic acid is boiled with aqueous strontium hydroxide, carbonic anhydride is eliminated with formation of *mesorcinol*, $C_9H_{12}O_2$.

From *Cetraria juniperina var. pinastri* or *Evernia pinastri* (? prunastri) the author has isolated a compound which he terms *chrysocetraric acid*; it melts at 178°, and the analysis agrees with the formula $C_{19}H_{14}O_6$, but in other respects it closely resembles pinastric acid described by Zopf (preceding abstract), who obtained it from *Cetraria pinastri* and *C. juniperina*.

On extracting *Parmelia parietina* (Ach.) or *Physcia parietina* (Schaer) with ether, a compound is obtained which the author proposes to call *physcion*, this name being selected in preference to chrysophyscin (Abstr., 1894, i, 541) and fiscic acid (Abstr., 1882, 1083), owing to its quinonic character and to the fact that the colour is brick-red instead of golden. Physcion, $C_{16}H_{12}O_5$, melts at 207°; the alcoholic solution is neutral. With alcoholic potash it forms a bluish-violet, amorphous *compound*, $C_{16}H_{12}O_5,2KOH$, which yields the *compound* $C_{16}H_{12}O_5,KOH$ on treatment with water; this crystallises in purple needles, and both substances are decomposed by water and carbonic anhydride. Physcion does not combine with hydroxylamine, but it forms a crystalline *compound* with phenylhydrazine. The *diacetyl* derivative crystallises in greenish-yellow needles, and melts at 183°; the *benzoyl* and *dibenzoyl* derivatives melt at 171° and

230° respectively. The *mononitro*-derivative crystallises from glacial acetic acid in small orange needles, and melts at 210°; the solution in ammonia is red, and the *sodium* salt forms cherry-red needles. The *dinitro*-derivative melts at 96°, and gives rise to highly-coloured salts.

Protophyscion, $C_{15}H_{10}O_5$, is obtained by heating physcion with hydriodic acid; it forms lustrous, brown needles, and melts at 198°.

Physconic acid, $C_{16}H_8O_6$, is formed when physcion is fused with potash; it is a bluish-black powder which decomposes without previous fusion. It resists the action of hydriodic acid and of acetic anhydride.

On adding zinc dust to a solution of physcion in glacial acetic acid, a compound, $C_{16}H_{14}O_5$, is formed which the author terms *physcihydrone;* it crystallises in pale, yellow needles, and melts at 180—182°. Fuming hydriodic acid converts it into *protophyscihydrone*, $C_{15}H_{12}O_5$, which melts at 210°.

In addition to physcion, the lichen from which it is derived contains physcianin and physciol. *Physcianin*, $C_{10}H_{12}O_4$, forms colourless prisms, and melts at 143°; at high temperatures it sublimes. An alcoholic solution is coloured bluish-violet by ferric chloride, whilst calcium hypochlorite develops a blood-red coloration which disappears when more of the reagent is added. *Physciol*, $C_7H_8O_3$, crystallises in slender, colourless needles; it melts at 107°, and volatilises at higher temperatures. An alcoholic solution becomes greenish-black on addition of ferric chloride, whilst calcium hypochlorite produces a yellowish-brown coloration. M. O. F.

Sulphides and Hydrosulphides of Aromatic Bases. By ALBERT EDINGER (*J. pr. Chem.*, 1895, [2], **51**, 91—96).—When quinoline benzyl chloride is treated with sodium hydrosulphide in concentrated aqueous solution, a white precipitate is produced which rapidly decomposes in the air. It has the formula $C_9NH_7(C_7H_7)\cdot SH$, and when rapidly dissolved in ether and treated with alcoholic platinic chloride in a freezing mixture yields a substance, $(C_{16}H_{15}NS)_2,PtCl_4$, as a pale yellow precipitate, decomposing at 223°. Quinoline benzyl chloride reacts with potassium sulphide in a similar manner, yielding a substance of the formula

$$[C_9NH_7(C_7H_7)]_2S,$$

which also reacts with platinic chloride, forming a brown substance of the formula $S(C_{16}H_{14}N)_2,PtCl_4$, which decomposes at 228°. When boiled with alcohol, both of these bases are converted into the same red, amorphous, comparatively stable substance which has the composition $C_{16}H_{15}NS$, but is not identical with the compound described above. When the quinoline benzyl chloride is treated with potassium mercaptide, a light, yellow, unstable oil is obtained which yields a *platinum* compound, $[C_9H_7N(C_7H_7)SEt]_2,PtCl_4$, melting at 219°.

A. H.

Iodisoquinoline. By ALBERT EDINGER (*J. pr. Chem.*, 1895, [2], **51**, 204—210).—*Isoquinoline tetriodide* is prepared by dissolving iodine (4 atoms) in carbon bisulphide and adding the solution to one

of isoquinoline (1 mol.) in the same solvent; after a time, dark blue crystals melting at 130° separate. It is freely soluble in alcohol and acetone, but only very sparingly in chloroform, ether, or carbon bisulphide; it loses iodine when exposed to air.

Iodisoquinoline diiodide, $C_9IH_6I_2N$, is obtained by heating isoquinoline (10 grams) with iodine (20 grams), iodic acid (5 grams), and water (200 c.c.) in a reflux apparatus for $1\frac{1}{2}$ hours. The oily product crystallises from alcohol, and melts at 101°. When its aqueous solution is treated with sulphurous acid, it yields *iodisoquinoline hydriodide*, which crystallises in light brown needles, and melts at 173°. From this, *iodisoquinoline* is obtained by treatment with caustic soda; it crystallises in white needles, melts at 99°, and is sparingly soluble in water, but freely in organic solvents; it sublimes and distils, resembling aromatic amines in all the usual reactions. The *methiodide* (m. p. 258—259°), *platinochloride*, with $2H_2O$, *picrate* (m. p. 206°), and *chromate* (m. p. 190°) are described. *Nitro-iodisoquinoline* melts at 140°. On oxidation, iodisoquinoline yields phthalic acid, showing that the iodine must be in the pyridine ring.

A. G. B.

Pyridazine. By Ernst Täuber (*Ber.*, 1895, **28**, 451—455).—When phenazone, $C_6H_4<\overline{N:N}>C_6H_4$ (Abstr., 1892, 184), is suspended in water and oxidised with potassium permanganate on the water bath, it yields *pyridazinetetracarboxylic acid*,

$$\begin{array}{l} COOH\cdot C \text{——} C\cdot COOH \\ COOH\cdot C\cdot N:N\cdot C\cdot COOH \end{array},$$

the *dipotassium salt* of which separates out when the filtered and concentrated solution is acidified with hydrochloric acid; it crystallises in white needles. If this salt is dissolved in cold, 15 per cent. hydrochloric acid, lustrous, rhombohedral crystals of a *monopotassium salt*, with $1H_2O$, soon separate. When heated for two hours with hydrochloric acid on the water bath, it loses carbonic anhydride, and, if the solution is concentrated and then diluted with water, *pyridazinedicarboxylic acid*, probably $\begin{array}{l} N\cdot CH:C\cdot COOH \\ N\cdot CH:C\cdot COOH \end{array}$, separates; this crystallises in colourless prisms, darkens just above 200°, and melts and decomposes at 205°. When it is heated for 12 hours with 5 per cent. hydrochloric acid at 200°, it yields *pyridazine*, $\begin{array}{l} N\cdot CH:CH \\ N\cdot CH:CH \end{array}$; this is a mobile, colourless oil which boils at 208° (corr.) and melts at −8°; it mixes with water in all proportions, and dissolves readily in alcohol, benzene, and ether, but not in light petroleum; it has a feeble odour suggestive of pyridine; it is neutral to litmus, and forms, for the most part, soluble salts; the *gold chloride compound*, $C_4H_4N_2,AuCl_3$ (the compound containing HCl in addition is unstable), however, separates even from dilute solutions in tiny, lemon-yellow needles which melt and decompose at about 110°; mercuric chloride also forms an insoluble compound, but the platinochloride only separates from concentrated solutions of the base or its hydrochloride.

C. F. B.

Pyrazole Series. By R. von Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 43—79).—A detailed account of researches of which notices have already been published (compare Abstr., 1893, i, 180, 367, 428, 611, 729; 1894, i, 145, 260, 349, 350, 385). A. H.

Pyridazolones. By R. v. Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 140—157; compare Abstr., 1893, i, 368, 732).—The preparation of pyridazolone* has been already described (Abstr., 1893, i, 732). The compound boils at 169·5—171°, and is less prone to enter into reactions than is pyrazolone; with silver nitrate and ammonia in alcoholic solution, it gives a white, amorphous precipitate of the *silver*-derivative $C_4H_5N_2OAg$.

The derivatives of *pyridazolone-4-carboxylic acid*,

$$NH<\begin{matrix}N=CH\\CO\cdot CH_2\end{matrix}>CH\cdot COOH,$$

were previously mis-described as those of pyridazolone-3-carboxylic acid (*loc. cit.*). The acid itself is a crystalline mass which melts above 250°, and dissolves in the usual solvents; the *silver*, *calcium* (with $1H_2O$), *barium* (with $2\frac{1}{2}H_2O$), *lead*, *copper* (with $1\frac{1}{2}H_2O$), *methylic* (m. p. 209—210°), and *ethylic* (m. p. 172°) salts are described. *Pyridazolone-4-carbonylhydrazine*, $NH<\begin{matrix}N=CH\\CO\cdot CH_2\end{matrix}>CH\cdot CO\cdot NH\cdot NH_2$, and its corresponding *benzylidene* derivative,

$$NH<\begin{matrix}N=CH\\CO\cdot CH_2\end{matrix}>CH\cdot CO\cdot NH\cdot N:CHPh,$$

have been described as 3-derivatives (*loc. cit.*). *Pyridazolone-4-carbonylisopropylenehydrazine*, $NH<\begin{matrix}N=CH\\CO\cdot CH_2\end{matrix}>CH\cdot CO\cdot NH\cdot N:CMe_2$, is obtained by dissolving the carbonylhydrazine in acetone; it crystallises from the solution in small needles and prisms which melt above 250°. 3-*Phenylpyridazolone*, $NH<\begin{matrix}N:CPh\\CO\cdot CH_2\end{matrix}>CH_2$, is prepared by heating ethylic β-benzoylpropionate with hydrazine hydrate in alcohol; it crystallises in large, flat needles, and melts at 145°; with benzaldehyde, it gives a red, easily soluble colouring matter; with nitrous acid, it yields a yellow, unstable *nitroso*-compound, which melts at 124°.

The author describes phthalazone (Abstr., 1893, i, 372) under the name *phenopyridazolone*. When heated with methylic iodide and methylic alcohol, it yields 1-*Methylphenopyridazolone*, $C_6H_4<\begin{matrix}CH:N\\|\\CO\cdot NMe\end{matrix}$, which crystallises in laminæ or prisms, and melts at 114°; it has no acid properties. 1-*Ethylphenopyridazolone* crystallises in yellow laminæ and melts at 67—68°.

6-*Methoxyphenopyridazole*, $C_6H_4<\begin{matrix}CH=N\\|\\C(OMe):N\end{matrix}$, obtained from the interaction of 6-chlorophenopyridazole and sodium methoxide, crys-

* Curtius has recently called derivatives of this class pyridazinones (this vol., 1, 247).

tallises in needles, and melts at 60—61°. The corresponding *ethoxy*-derivative melts at 29—31°.

1-*Acetylphenopyridazolone*, made by heating pyridazolone with acetic anhydride, crystallises in needles or prisms, and melts at 135°. *Phenopyridazolonecarboxylic acid*, $C_6H_4<\begin{matrix}C(COOH):N\\ CO\text{———}NH\end{matrix}$, is obtained by warming hydrazine hydrate with benzoylformic-orthocarboxylic acid in alcohol, melts above 250°; its *silver*, *copper* (with $1H_2O$), and *methylic* salts are described.

3-Phenylphenopyridazolone (Abstr., 1893, i, 368) melts at 236°. 1-*Methyl*-3-*phenylphenopyridazolone* crystallises in laminæ, melts at 153°, and distils unchanged. 1-*Ethyl*-3-*phenylphenopyridazolone* melts at 109° and distils unchanged; 1-*Acetyl*-3-*phenylphenopyridazolone* melts at 178—179°.

3-*Paratolylphenopyridazolone* is prepared from paratoluoylbenzoic acid and hydrazine hydrate; it melts at 246°, and boils unchanged. 1-*Methyl*-3-*paratolylphenopyridazolone* crystallises in laminæ and melts at 170°. 3-*Xylylphenopyridazolones* are obtained when the three xyloylbenzoic acids are heated with hydrazine hydrate respectively; they melt above 250° and distil unchanged. 3-*Naphthylphenopyridazolones* have also been prepared.

The discovery of the isomeric alkyl derivatives of phenopyridazolone points to the existence of the tautomeric forms $CO<\begin{matrix}NH\text{—}N\\ CH_2{\cdot}CH_2\end{matrix}>CH$ and $C(OH)<\begin{matrix}N\text{——}N\\ CH_2{\cdot}CH_2\end{matrix}>CH$. A distinction between pyrazolones and pyridazolones resides in their behaviour towards acids; the former are very stable, whilst the latter are easily split up into their parent substances. On the other hand, the pyridazolones can be distilled unchanged, whilst the pyrazolones, with the exception of pyrazolone itself and some of the simpler derivatives, are decomposed by distillation. The pyrazolones yield isonitroso-derivatives with nitrous acid, and azo-compounds with diazobenzene salts; the pyridazolones do not show either reaction. A. G. B.

Isomerism in the Pyrazole Series. By R. v. Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 157—164).—The author agrees with Buchner (this vol., i, 192) that the phenylpyrazole which melts at 228° cannot be the 4-derivative, as Knorr and Sjollema have stated it to be (Abstr., 1894, i, 546). Stolz (Abstr., 1894, i, 259) has expressed his opinion that the author's phenylpyrazolone (*Ber.*, 1893, **26**, 2974), which melts at 155°, is not 1-phenyl-5-pyrazolone, but on grounds which are shown to be insufficient. If, as has been stated in certain German patent specifications, the so-called "pseudoantipyrines," $CO<\begin{matrix}NR_1{\cdot}NPh\\ CH:CR_{11}\end{matrix}$, are poisonous, whilst the antipyrines, $CO<\begin{matrix}NPh{\cdot}NR_1\\ CH:CR_{11}\end{matrix}$, can be used as antipyretics, it becomes of great importance to be able to state the exact conditions under which compounds of the one and of the other class are produced.

C. Walker has prepared some pyrazolonesulphonic acids to which he ascribes the formula $NPh<\begin{matrix}N(SO_3H)\cdot CMe\\ CO\text{———}CR\end{matrix}$ (Abstr., 1894, i, 475); this constitution is, however, exceedingly improbable, and the acids may be regarded as $CO<\begin{matrix}N(C_6H_4\cdot SO_3H)\cdot N\\ CHR\text{———}CMe\end{matrix}$. A. G. B.

Aromatic Glyoxaline Compounds. By RICHARD ANSCHÜTZ (*Annalen*, 1895, **284**, 8).—Condensation of α-hydroxyketones with thiocarbamide or ammonium thiocyanate, and with carbamide, has already been studied (Abstr., 1891, 725); the two following abstracts contain a further description of some of the products. M. O. F.

Constitution of Products obtained from Benzoïn by the Action of Thiocarbamide or Ammonium Thiocyanate, and Carbamide. By RICHARD ANSCHÜTZ and K. SCHWICKERATH (*Annalen*, 1895, **284**, 9—25; compare Abstr., 1891, 725).—The orientation adopted by the authors for glyoxaline compounds is expressed by the formula $\begin{matrix}\alpha R\cdot C\cdot \overset{\nu}{N}R\\ \| \quad\quad >C\cdot R\mu.\\ \beta R\cdot C\text{—}N\end{matrix}$

αβ-Diphenylglyoxaline μ-hydrosulphide is obtained by condensing benzoïn with thiocarbamide or ammonium thiocyanate; the *sodium* salt forms lustrous, pale yellow leaflets. Solutions in acetic acid and alcohol exhibit a feeble, violet fluorescence. Treatment with concentrated sulphuric acid gives rise to evolution of sulphurous anhydride with development of a cherry-red coloration, a yellow, amorphous substance being formed on application of heat. This product again becomes red in a vacuum, but is decolorised on exposure to the air; it dissolves in alkali carbonates, and the solution becomes gelatinous.

αβ-Diphenylglyoxaline μ-methosulphide, $\begin{matrix}CPh\cdot NH\\ \| \quad\quad >C\cdot SMe,\\ CPh\text{—}N\end{matrix}$ is obtained from the hydriodide by treatment with boiling water. It crystallises from dilute alcohol in slender, white needles which melt at 233—234°; when it is fused with potash, the odour of mercaptan becomes perceptible. The *hydriodide* is formed when diphenylglyoxaline hydrosulphide is heated with methylic iodide and methylic alcohol on the water bath. It forms colourless crystals belonging to the rhombic system; $a : b : c = 0{\cdot}90199 : 1 : 0{\cdot}72716$. These crystals contain 1 mol. $CH_3\cdot OH$, which is lost on exposure to the air. The hydriodide becomes reddish-brown at 180—190°, and melts at 201—202°.

αβ-Diphenylglyoxaline μ-ethosulphide, crystallises from alcohol in small, white needles, and melts at 181—182°.

αβ-Diphenylglyoxaline μ-disulphide, $S_2(C_3N_2HPh_2)_2$, is obtained from the sodium salt of αβ-diphenylglyoxaline μ-hydrosulphide by the action of iodine, or by oxidation with potassium permanganate; it crystallises from alcohol in golden-yellow needles.

αβ-Diphenylglyoxaline-μ-sulphonic acid is produced by further oxidation of the foregoing substance with potassium permanganate; it

melts at 271—273° with decomposition, and crystallises in white needles which contain $1H_2O$. The sulphonic acid resists the action of concentrated hydrochloric acid at 180—200°. The *potassium* salt forms small, white crystals.

When $\alpha\beta$-diphenylglyoxaline μ-hydrosulphide is oxidised with nitric acid, the chief product is benzile; if, however, a mixture of sulphuric acid and potassium dichromate is used, dibenzoylcarbamide is formed. Dibenzoylcarbamide yields carbonic anhydride, benzonitrile, and benzamide when heated at 205—210°.

Diphenylacetyleneureïn, or *tolaneureïn*, $\begin{matrix}CPh\cdot NH\\ \|\\ CPh\cdot NH\end{matrix}\!\!>\!CO$, is soluble in warm aqueous soda, and also resembles $\alpha\beta$-diphenylglyoxaline μ-hydrosulphide in its behaviour towards concentrated sulphuric acid; it resists, however, the action of acetic chloride, and does not form additive products with methylic and ethylic iodides. Potassium permanganate oxidises it to a mixture of benzoic and benzilic acids, whilst chromic acid gives rise to dibenzoylcarbamide.

$\alpha\beta$-Diparamethoxyphenylglyoxaline μ-hydrosulphide,

$$\begin{matrix}OMe\cdot C_6H_4\cdot C\cdot NH\\ OMe\cdot C_6H_4\cdot C\!-\!N\end{matrix}\!\!>\!C\cdot SH,$$

is produced by condensation of anisoïn with thiocarbamide; it melts at 280°, and becomes yellowish-green on treatment with concentrated sulphuric acid.

Diparamethoxytolaneureïn, $\begin{matrix}OMe\cdot C_6H_4\cdot C\cdot NH\\ \|\\ OMe\cdot C_6H_4\cdot C\cdot NH\end{matrix}\!\!>\!CO$, is obtained by condensing anisoïn with carbamide; it crystallises from alcohol in small, white needles, and remains unchanged at 280°. M. O. F.

Action of Monosubstituted Derivatives of Carbamide and Thiocarbamide on Benzoïn. By Richard Anschütz and Hermann Müller (*Annalen*, 1895, **284**, 25—35).—*$\alpha\beta$-Diphenyl-ν-ethylglyoxaline μ-hydrosulphide*, $\begin{matrix}CPh\cdot NEt\\ \|\\ CPh\!-\!N\end{matrix}\!\!>\!C\cdot SH$, is prepared by heating a mixture of ethylthiocarbamide, benzoïn, and alcohol for four hours at 180—190°; it crystallises in yellowish needles, and undergoes no change at 240°. *$\alpha\beta$-Diphenyl-ν-ethylglyoxaline μ-methosulphide* melts at 106°.

$\alpha\beta$-Diphenyl-ν-allylglyoxaline μ-hydrosulphide crystallises in needles, and remains unchanged at 240°; the *potassium* salt forms lustrous leaflets.

$\alpha\beta\nu$-Triphenylglyoxaline μ-hydrosulphide is obtained by condensing benzoïn with phenylthiocarbamide. It crystallises from alcohol or glacial acetic acid in white leaflets, and does not melt below 290°; the solutions in these two solvents exhibit a violet fluorescence. The *potassium* salt forms stellate groups of colourless needles.

$\alpha\beta\nu$-Triphenylglyoxaline μ-methosulphide crystallises from alcohol in colourless needles and melts at 177°; on fusing it with potash, the odour of mercaptan becomes perceptible. *$\alpha\beta\nu$-Triphenylglyoxaline μ-ethosulphide* forms yellow crystals. *$\alpha\beta$-Diphenyl-ν-β-naphthylglyoxaline μ-hydrosulphide* is prepared by heating a mixture of β-naphthyl-

thiocarbamide, benzoïn, and alcohol for five hours at 200—210°; it crystallises from alcohol in small, colourless needles.

Diphenylacetylenemethylureïn, $\begin{matrix}CPh\cdot NMe\\ \|\\ CPh\text{——}N\end{matrix}>CO$, is produced when benzoïn is heated with methylcarbamide and alcohol for several hours at 270—280°. It forms white needles, and remains unchanged at 290°.

Diphenylacetylenephenylureïn also undergoes no change at 290°, and *diphenylacetylene-β-naphthylureïn*, which crystallises in grey needles, becomes brown at 280°. M. O. F.

Phenometadiazine Derivatives. By STEFAN NIEMENTOWSKI (*Ber.*, 1895, **28**, 443).—The author points out that between the melting point of β-ethyl-α-hydroxyphenometadiazine and of phenoβ-isopropyl-α-hydroxymetadiazine as determined by him, and the observations recorded in the recent paper of Bischler and Lang (this vol., i, 250), a wide discrepancy exists; the compounds in question may occur in two isomeric forms. M. O. F.

Orthamidobenzylamine. By MAX BUSCH (*J. pr. Chem.*, 1895, [2], **51**, 113—139).—The majority of the reactions and compounds described in this paper has already received notice (Abstr., 1894, i, 146, 625; this vol., 31).

Oxidation of ketotetrahydroquinazoline and of thiotetrahydroquinazoline with potassium permanganate, produces benzoylenecarbamide. When reduced by sodium in alcohol, thiotetrahydroquinazoline yields tetrahydroquinazoline, the *hydrochloride*, $C_8H_{10}N_2,HCl$, of which is not dissociated by water, as are those of its substituted derivatives, and melts at 192°; the *platinochloride* is described.

Orthamidobenzylmethylamine *hydrochloride*, $C_8H_{12}N_2,2HCl$, crystallises in lustrous laminæ, and melts at 217°.

3-*Methylthiotetrahydroquinazoline*, $C_6H_4<\begin{matrix}NH\cdot CS\\ |\\ CH_2\cdot NMe\end{matrix}$, prepared by heating orthamidobenzylmethylamine with carbon bisulphide, crystallises in white needles, melts at 181°, and dissolves easily in benzene and chloroform, but only sparingly in ether and water.

Methyldihydro-β-phenotriazine hydrochloride crystallises in large, pale, yellow prisms, and melts at 146—147°, evolving gas; the *platinochloride* and *picrate* are described.

Orthamidobenzylethylamine hydrochloride, $C_9H_{14}N_2,2HCl$, melts at 210°; the *oxalate* at 184°. When the base is treated in ethereal solution with a 20 per cent. solution of phosgene in toluene, 3-*ethylketotetrahydroquinazoline* is obtained; this crystallises in white needles, and melts at 142°.

Ethyldiketotetrahydroquinazoline, $C_6H_4<\begin{matrix}NH\cdot CO\\ |\\ CO\cdot NEt\end{matrix}$, is the product of the oxidation of ethylthiotetrahydroquinazoline by potassium permanganate; it crystallises in lustrous, white needles, melts at 188°, and dissolves in hot absolute alcohol and in aqueous alkalis, to which it imparts a blue fluorescence. It is, perhaps, identical with Söderbaum's phenoethyldiketometadiazine (Abstr., 1890, 1254).

1 : 3-*Methylethylthiotetrahydroquinazoline*, $C_6H_4<\begin{matrix}NMe\cdot CS\\ |\\ CH_2\cdot NEt\end{matrix}$, is prepared by heating ethylthiotetrahydroquinazoline with methylic alcohol and methylic iodide. It forms a yellow oil which gradually crystallises from alcohol in square tablets, melting at 65°.

The *hydrochloride*, $C_9H_{11}N_3,HCl$ (m. p. 141°), *platinochloride*, *hydrobromide* (m. p. 151°), *sulphate*, $C_9H_{11}N_3,H_2SO_4$ (m. p. 150°), and *picrate* (m. p. 150°) of β-phenomethyldihydrotriazine are described.

A. G. B.

Orthamidobenzylamine. By MAX BUSCH (*J. pr. Chem.*, 1895, [2], **51**, 257—284; compare Abstr., 1894, i, 146).—*Orthonitrotribenzylamine* is formed when benzylic chloride is heated with orthonitrobenzylamine (2 mols.); it crystallises in large, sulphur-yellow prisms, and melts at 56°. The *hydrochloride* melts at 190°, and the *platinochloride* at 200°. *Orthonitrodibenzylamine* is obtained by heating benzylic chloride with nitrobenzylamine in alcoholic solution. It is a yellowish oil, and its *hydrochloride* melts at 225°.

Orthonitrobenzylanilidophenylsulphone, $NO_2\cdot C_6H_4\cdot CH_2\cdot NPh\cdot SO_2Ph$, is obtained by heating nitrobenzylamine with benzenesulphonic chloride, and crystallises in needles melting at 143°.

Orthamidobenzylanilidophenylsulphone crystallises in matted needles, and melts at 139—140°. It does not yield an anhydro-compound when heated alone or with dehydrating agents. Hydrochloric acid decomposes it with formation of phenylsulphanilide.

Phenylketotetrahydroquinazoline (Abstr., 1892, 1495) and phenylthiotetrahydroquinazoline are converted by oxidation with potassium permanganate into *phenyldiketotetrahydroquinazoline*, $C_6H_4<\begin{matrix}NH\cdot CO\\ |\\ CO\cdot NPh\end{matrix}$, which crystallises in arborescent needles, and melts at 272°. Phenylthiotetrahydroquinazoline is converted by methylic iodide into the *hydriodide of methylphenylthiotetrahydroquinazoline*, which melts and decomposes at 225°. The free *base* forms compact crystals melting at 92°, and is strongly basic, whereas the unmethylated quinazoline is indifferent towards acids.

Orthonitrobenzylparatoluidophenylsulphone forms compact yellow crystals which melt at 124°. The corresponding *amido-compound* crystallises in lustrous, white needles, and melts at 132°.

Orthamidobenzylorthotoluidine, $NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Me$, crystallises in flat, lustrous needles melting at 94°. The *hydrochloride* melts at 180—181°. During the reduction of orthonitrobenzylorthotoluidine, *orthotolylindazole*, $C_6H_4<\begin{matrix}N\\ |\\ CH\end{matrix}>N\cdot C_6H_4Me$, which crystallises in slender needles, melting at 80—81°, is obtained accompanied by *orthazobenzylorthotoluidine*, $N_2(C_6H_4\cdot CH_2\cdot NH\cdot C_7H_7)_2$, which forms red crystals melting at 160°. Orthamidobenzylorthotoluidine does not appear to react with nitrous acid to form a phenotriazine. *Orthotolylketotetrahydroquinazoline* crystallises in lustrous, white plates, and melts at 189—190°. *Orthotolylthiotetrahydroquinazoline* forms flat, white needles, and melts at 202°. *Orthotolyldiketotetrahydroquinazoline*, obtained by oxidation from the foregoing compounds, forms

white crystals melting at 241—242°. *Orthonitrobenzylorthotolylnitrosamine* crystallises in yellowish, vitreous needles, and melts at 64—65°. The *amido-compound* melts at 86—87°. Acetyldihydro-β-phenotriazine is decomposed by hydrochloric acid with formation of *orthochlorobenzylacetamide*, which crystallises in white, lustrous needles melting at 79—80°. The *hydrochloride* also forms white needles. Both acetyldihydrophenotriazine and its salts form azo-compounds by condensation with amido-compounds and phenols. With β-naphthol, a compound which crystallises in slender, orange-red needles is formed, whilst the product obtained from dimethylaniline is dark yellow, and that from metaphenylenediamine, golden-yellow.

Benzoyldihydro-β-phenotriazine is decomposed by the halogen hydr-acids with formation of the corresponding substituted benzylbenzamides. *Orthoch orobenzylbenzamide* forms colourless, lustrous needles melting at 116—117°. *Orthobromobenzylbenzamide* crystallises in plates melting at 134°, whilst *orthiodobenzylbenzamide* also forms plates which melt at 154°. *Orthohydroxybenzylbenzamide* may be obtained by boiling the benzoyldihydrophenotriazine hydrochloride with water, and forms white needles melting at 139—140°. The benzoyltriazine condenses with β-naphthol to form the *compound* $COPh{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH$, which crystallises in silky, purple-red needles melting at 215°. On reduction, it is converted into orthamidobenzylbenzamide and amidonaphthol. The *compound* with dimethylaniline is orange-yellow, and melts at 140°; whilst that with metaphenylenediamine is also orange-yellow, and decomposes and melts at 160°. A. H.

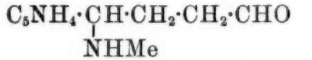
New Synthesis of Triazole and its Derivatives. By Guido Pellizzari (*Gazzetta*, **24**, ii, 222—229).—The alkylic derivatives of formylhydrazide react readily with formamide yielding mono-substituted triazoles and water. In the preparation of triazole or of 1-phenyltriazole, formamide is slowly distilled with formylhydrazine or formylphenylhydrazine respectively; the triazole distils, and a good yield is obtained on purification. In the preparation of triazole, a poorer yield is obtained by distilling hydrazine hydrate or hydrochloride with formamide or ammonium formate, or by heating hydrazine hydrochloride with ammonium chloride or sodium formate, inasmuch as secondary reactions occur to a greater extent than in the first method described above. W. J. P.

Nicotine. By Adolf Pinner (*Ber.*, 1895, **28**, 456—465; compare Abstr., 1891, 473, and 1892, 1010).—It is shown that oxynicotine, $C_{10}H_{14}N_2O$ (*not* H_{12}), is not the primary product of the oxidation of nicotine with hydrogen peroxide, but is formed by condensation from an aldehyde first formed. When oxynicotine is heated for 8—10 hours at 140° with saturated baryta water, and the product distilled with steam, the distillate contains nicotine and pseudonicotine oxide, better named *nicotol*. From the residue, an oil can be isolated, which decomposes when heated at about 165° under 50 mm. pressure; by fractional crystallisation of the mixed picrates

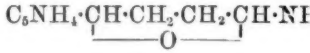
obtained from the oily distillate, nicotine and *nicotone*, an isomeride of oxynicotine and nicotol, were isolated. Nicotone is a colourless, strongly basic oil, which boils at 253°; it has no reducing action. The picrate, $C_{10}H_{14}N_2O,2C_6H_3N_3O_7$, melts at 184°, and is readily soluble in hot, but only sparingly in cold, water.

When metanicotine is treated with methylic iodide (3 mols.) in methyl alcoholic solution at the ordinary temperature, a *methiodide* of *methylmetanicotine*, $C_{10}H_{13}MeN_2,2MeI$, is obtained; this crystallises in colourless needles, and melts at 189°.

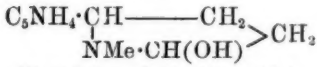
The following formulæ are assigned to the substances described in this and the previous papers. Brühl finds that those given for nicotine and metanicotine are in harmony with the optical constants of these substances as determined by him.



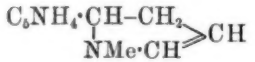
Aldehyde (Oxynicotine).



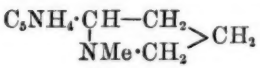
Nicotone.



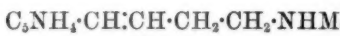
Nicotol (pseudonicotine oxide).



Dehydronicotine.



Nicotine.



Metanicotine.

C. F. B.

Nicotine Oxalate and other Salts. By H. Parenty and E. Grasset (*Compt. rend.*, 1894, **119**, 1273—1276).—Nicotine quadroxalate, $C_{10}H_{14}N_2,2H_2C_2O_4$, is readily obtained in nacreous lamellæ by adding excess of oxalic acid to the normal oxalate, $2C_{10}H_{14}N_2,H_2C_2O_4$. In order to prepare it on a large scale, the aqueous extract from tobacco residues is made alkaline, and allowed to fall in the form of fine rain through light petroleum, contained in a series of six vertical tubes in a special apparatus, the liquid passing through the six tubes in succession. The light petroleum is then vigorously agitated with the proper proportion of finely-powdered oxalic acid, and the quadroxalate is dried.

Nicotine quadroxalate is very soluble in water and in alcohol. When the anhydrous salt is heated, it melts at 110°, and begins to decompose with violent evolution of gas at 113·5°. At 160°, it yields the normal oxalate, and at 250° pure nicotine. In order to obtain the base, it is best, after the initial evolution of gas has moderated, to collect the distillate, and rectify it after adding calcium or lead oxide. The quadroxalate can be employed for the same purposes as nicotine. The fatal dose of free nicotine, when injected hypodermically, is 20 to 21 milligrams per kilo. of body weight, but this rises to 70 milligrams (or 150 milligrams of the quadroxalate) when the nicotine is in combination. It follows that the quadroxalate has only one-eighth of the poisonous effect of an equal weight of free nicotine. The physiological effects, though less intense, are identical.

C. H. B.

Diacetylcreatine and Benzylideneacetylcreatinine. By EMIL ERLENMEYER, jun. (*Annalen*, 1895, **284**, 49—52).—*Diacetylcreatine*, $C_4H_7O_2N_3Ac_2$, is obtained by dissolving creatine in excess of warm acetic anhydride and evaporating the liquid after addition of water; it crystallises from alcohol in slender needles, which melt at 165°.

Benzylideneacetylcreatinine, $C_{13}H_{13}O_2N_3$, is formed when creatine is heated on the water bath with benzaldehyde (1 mol.) and acetic anhydride (3 mols.); it crystallises from glacial acetic acid in small, golden-yellow needles, and melts at 213°.

The structure of the two foregoing compounds is probably represented by the expressions $\begin{matrix}\text{NMe·C(NHAc):NH}\\ |\\ \text{CH}_2\text{·COOAc}\end{matrix}$ and

$$\begin{matrix}\text{CO}\text{———}\text{NBz}\\ |\\ \text{C(CHPh)·NMe}\end{matrix}\!\!>\text{C:NH}$$

respectively. M. O. F.

β-Hydroxycinchonine. By EMILIE JUNGFLEISCH and E. LÉGER (*Compt. rend.*, 1894, **119**, 1268—1270).—β-Hydroxycinchonine (see Abstr., 1889, 906) is formed, together with α-hydroxycinchonine, by the prolonged action of sulphuric acid diluted with an equal weight of water on cinchonine, at 120°. The α-compound is separated in the form of basic hydrochloride, which is only slightly soluble, and the β-derivative in the form of basic succinate. Final purification is effected by conversion into diacetyl derivatives, that derived from β-hydroxycinchonine being only very slightly soluble in ether.

β-Hydroxycinchonine crystallises from strong alcohol in small, colourless, anhydrous, acicular prisms which begin to decompose at 250° and melt at 273° (corr.). It is somewhat more dextrogyrate than the α-compound; in absolute alcohol at 17°, $[\alpha]_D = +188{\cdot}8°$; in water containing 2 mols. HCl at 15°, $[\alpha]_D = +228°$; and with 4 mols. HCl, $[\alpha]_D = +228{\cdot}33°$.

β-Hydroxycinchonine is almost insoluble in water, but in dilute solutions precipitation by an alkali takes place very slowly; it is soluble in alcohol, especially on heating, but is less soluble in acetone than its isomeride; it dissolves in chloroform, especially at the moment of its liberation from one of its salts, although the excess of base thus dissolved gradually separates in a crystalline form. The base is alkaline to litmus and phenophthalein, and forms two series of salts, normal $C_{38}H_{22}N_2O_4,2HR'$ and $C_{38}H_{22}N_2O_4,HR'$. They crystallise well in prisms or needles, and with the exception of the basic iodide, platinochloride, cadmiochloride and basic oxalate, basic succinate and basic tartrate, are soluble in water, especially on heating. The *platinochloride* forms orange-yellow needles; the other salts are white.

C. H. B.

Hygrine and Hygric acid. By CARL T. LIEBERMANN and GUSTAV CYBULSKI (*Ber.*, 1895, **28**, 578—585).—In addition to the "low-boiling hygrine" and "high-boiling hygrine," a third alkaloïd has been isolated from Bolivian cusco leaves, and the name *cuskhygrine* suggested for it. It is a colourless oily liquid, boils at 185° (32 mm.), has a sp. gr. of 0·9767 at 17°/17°, and is optically inactive. The

base, $C_{13}H_{24}N_2O$, is isolated by means of the crystalline *nitrate*. The *hydrochloride*, $C_{13}H_{24}N_2O,2HCl$, and the *aurochloride*,

$$C_{13}H_{24}N_2O,2HAuCl_4,$$

are crystalline, the former is hygroscopic. The *platinochloride* has also been obtained. "Low-boiling hygrine" boils at 92—94° (20 mm.) and 111—113° (50 mm.); sp. gr. = 0·935 at 17°/4°; $\alpha_D = -1·3°$.

Hygric acid melts at 164°, but retains water of crystallisation even when deposited from alcohol, hence the lower melting points previously observed (Abstr., 1891, 586). When the anhydrous acid is heated slightly above its melting point, carbonic anhydride is copiously evolved, and a mixture of bases is obtained equal to 46 per cent. of the original acid. The constituent of lowest boiling point is *n*-methylpyrrolidine, which is a strong base and absorbs water and carbonic anhydride from the atmosphere; its vapour, when inhaled, produces violent headache. The *platinochloride*, $(C_5H_{11}N)_2,H_2PtCl_6$, melts at 233°. The *picrate*, *potassiomercuric iodide*, and *mercurochloride* crystallise in needles; the first two are yellow. The above base differs from piperidine in giving no nitroso-derivative, no compound with carbon bisulphide, and no compound corresponding with benzoylpiperidine; it is a tertiary base, and readily combines with methylic iodide. Determinations by Herzig and H. Meyer's method show that *n*-methylpyrrolidine, "low-boiling hygrine," and hygric acid all contain one NMe group, cuskhygrine contains two. The readiness with which carbonic anhydride is eliminated from hygric acid suggests that the carboxyl group is in the α-position, "low-boiling hygrine," therefore, probably has the formula

$$NMe<\begin{matrix}CH(COEt)\\CH_2-CH_2\end{matrix}>CH_2.$$

J. B. T.

Alkaloïds of Lupinus Albus. By Arturo Soldaini (*L'Orosi*, **17**, 253—262; compare Abstr., 1893, i, 379, 739).—The deliquescent dextrorotatory alkaloïd extracted from the seeds of *Lupinus albus* yields a deliquescent *hydrogen sulphate*, $C_{15}H_{24}N_2O,H_2SO_4,H_2O$, melting at 178—179°; the *normal sulphate*, $(C_{15}H_{24}N_2O)_2,H_2SO_4$ (?), crystallises in micaceous scales melting at 82—83°. The *hydrogen tartrate*,

$$C_{15}H_{24}N_2O,H_6C_4O_6,$$

crystallises in hemihedral, anorthic crystals melting at 192—193°; $a:b:c = 1·0257:1:0·8160$. $\alpha = 89°\ 0'$, $\beta = 95°\ 13'$, $\gamma = 90°\ 39'$. An *iodine* additive compound, $C_{15}H_{24}N_2OI_3$, was also obtained in brown scales melting at 196—197°.

The isomeric inactive alkaloïd also yields a *hydrogen sulphate* melting at about 186°, but the normal sulphate is a syrup. The *hydrogen tartrate*, $C_{15}H_{24}N_2O,H_6C_4O_6,2\frac{1}{2}H_2O$, is obtained in hemimorphic monosymmetric crystals melting and decomposing at 184—185°; $a:b:c = 0·9157:1:1·0432$. $\beta = 82°\ 52'$.

Lupinidine does not seem to occur in the seeds of *Lupinus albus*.

W. J. P.

Pereiro Bark. By OSWALD HESSE (*Annalen*, 1895, **284**, 195—196; compare Abstr., 1894, i, 155, also Freund and Fauvet, this vol., i, 194).—The author has not met with a second variety of pereiro bark, and is of opinion that the source of vellosine cannot strictly be regarded as such. M. O. F.

Pectase and the Pectic Fermentation. By GABRIEL BERTRAND and ALFRED MALLÈVRE (*Compt. rend.*, 1894, **119**, 1012—1014, and 1895, **120**, 110—112).—According to Fremy, pectase is an unorganised ferment which causes the coagulation of vegetable juices rich in pectin, and which exists in a soluble form in the roots of the carrot and the beet, and in an insoluble form in apples and other acid fruits. The authors find that the coagulum produced by the action of the juice of carrots on a solution of pectin consists of calcium pectate and is not pectic acid as has been generally supposed; it is insoluble in dilute solutions of alkalis, but dissolves very readily in dilute hydrochloric acid, and the solution contains calcium which is not precipitated on adding excess of ammonia.

If the whole of the calcium is precipitated from the juice of carrots by adding exactly the required amount of potassium oxalate, and if pectin is entirely freed from calcium by treatment with dilute alcohol acidified with hydrochloric acid, no coagulation takes place on mixing the two solutions. The addition of a small quantity of a calcium salt causes almost immediate gelatinisation. Neither pectase nor calcium salts alone are able to coagulate pectin; the simultaneous presence of the two is essential. Barium and strontium salts have the same effect as calcium salts.

The action of the juice of carrots on a solution of pectin is greatly retarded by the presence of inorganic acids, and by malic, citric, or oxalic acid. With 0·088 gram of hydrochloric acid in 100 c.c., gelatinisation does not take place until after 40 hours; and with 0·1 gram of acid, the liquid does not gelatinise at all. It is noteworthy that many fruits at certain stages of their development contain proportions of acid considerably greater than those employed in these experiments.

The effect of acids is reduced by the presence of an increased proportion of pectase or of calcium salts. Pectic fermentation, in fact, depends on the relative proportions of pectase, calcium salts, and free acid. There is little doubt that this retarding influence of acids led Fremy to conclude that pectase is not present in the juice of apples and other acid fruits, and to suppose that it was present in an insoluble form in the solid part of the pulp. As a matter of fact, if the juice from apples, pears, &c., at various stages of development, is carefully neutralised, it readily coagulates the juice of carrots. The readier action of the pectase left in the pulp is due to the fact that the greater part of the acid has been removed. The authors find that the pectase precipitated by alcohol will redissolve in water if sufficient time is allowed and has not really become insoluble as Fremy supposed. The apparent inactivity of the precipitated pectase is due to the fact that the calcium salts which originally accompanied it are, to a large extent, left in the alcoholic liquid. C. H. B.

The Blue Iodide of Cholic acid. By FRITZ W. KÜSTER (*Zeit. physikal. Chem.*, 1895, **16**, 156—163).—In order to determine whether the blue compound of iodine and cholic acid is a true compound or a solid solution, a solution of the acid in alcohol was prepared, iodine added, and the cholic acid precipitated by water. The partition ratio of the iodine in the cholic acid and aqueous alcohol was then determined. The ratio for different amounts of iodine was not constant. When the quantity of iodine in the acid reached 28 per cent. it remained approximately constant. The blue substance appears to be therefore a compound which is easily and completely dissociated by water, and the solution tension of the iodine against water is equal to that of the iodine in a solution containing 0·020 gram per 100 c.c. The partition ratios of iodine in alcohol and carbon bisulphide were also determined, the presence of the acid being shown to have little effect on these numbers. The compound is, therefore, neither a solid solution nor a true chemical compound but a crystal structure analogous to that which the acid forms with water, alcohol, &c. L. M. J.

Iodine Compounds of Starch and of Cholic acid. By FRANZ MYLIUS (*Ber.*, 1895, **28**, 385—390; compare Abstr., 1887, 568, and Küster, this vol., i, 199).—Cholic acid has already been shown to yield blue compounds of the type $(C_{24}H_{40}O_5)_4,I_4,HI + nH_2O$ when it is treated with solutions of iodine in aqueous hydriodic acid or metallic iodides. It is now shown that if these solutions are concentrated as regards the iodide, a brown crystallised compound, $C_{24}H_{40}O_5,I_2$, is formed, into the composition of which neither hydriodic acid nor metallic iodides enter. This compound is regarded as a true iodine additive compound of cholic acid, the others are compounds of iodine with the hydriodide, &c., of the acid. The brown compound is best made by dissolving cholic acid and iodine (1 mol. of each) in alcohol, and diluting the solution with water. It is converted into the blue compound by the action of reducing agents or of hydriodic acid or metallic iodides in the presence of water, and it is formed from the blue compound when the latter is treated with concentrated iodine solutions.

Starch, under similar circumstances, also yields a brown compound, $(?\ C_{24}H_{40}O_{20} + I_2)$, in addition to the blue compound already known, and so do the amyloïds obtained from cellulose. C. F. B.

Phosphorcarnic acid. By MAX A. SIEGFRIED (*Ber.*, 1895, **28**, 515—519).—The author has previously shown (this vol., i, 76) that the muscles contain a compound termed phosphorcarnic acid which is easily separated by means of its iron compound, "carniferrin." By the action of baryta water, the acid is resolved into phosphoric acid and carnic acid, $C_{10}H_{15}N_3O_5$, which is identical with anti-peptone. The alcoholic mother liquor obtained after the deposition of the carnic acid contains succinic acid and sarcolactic acid; the former gave a soluble barium salt probably derived from the labile modification of the acid. By the action of sodium carbonate on carniferrin, and treatment of the filtrate with baryta water, phosphoric acid, carnic acid, and a sugar are formed; the latter readily reduces Fehling's

solution, and yields an osazone, but has not yet been identified. It is very probable that sarcolactic acid is formed by the hydrolysis of phosphorcarnic acid, and attempts will be made to prove this. The term *nucleon* is suggested for compounds, such as phosphorcarnic acid, which are allied to the nucleïns but contain peptone instead of albumin. Following Kossel, it is necessary to distinguish between *true nucleons* and *paranucleons;* phosphorcarnic acid belongs to the latter class and may be termed *muscle nucleone.*

Experiments on dogs have shown that phosphorcarnic acid is absorbed during muscular activity; in one instance three times as much was present in inactive muscles as in fatigued ones. This explains the appearance of phosphoric acid in the muscles as the result of their activity. As carnic acid has not hitherto been detected in the muscles, it is either absorbed during muscular growth or it contributes by its oxidation to muscular energy.

The formation of ammonium thiosulphate from ammonium sulphide and carnic acid which has been previously suggested as a test for the latter, only applies when colourless, recently prepared, ammonium sulphide is employed, as the yellow compound when evaporated alone yields ammonium thiosulphate. J. B. T.

Coagulation of Colloïds. By JOHN W. PICKERING (*Proc. Physiol. Soc.*, 1895, 5—6).—Colloïd substances prepared by Grimaux were examined, the three principal being those formed by the action of phosphorus pentachloride on metamidobenzoic acid, and that formed by the action of phosphorus oxychloride on aspartic acid.

In each case, the substance is a white amorphous powder readily soluble in ammonia; on evaporating the ammonia, brownish plates remain not unlike dried serum albumin. They are slightly soluble in distilled water in the cold, readily on heating. The solution is opalescent, and does not coagulate on heating; but if one or two drops of a 1 per cent. solution of a soluble salt of either barium, strontium, or calcium, is added, pronounced coagulation begins on heating to 70°. A few drops of a saturated solution of sodium chloride will also induce coagulation at 70°. If a more dilute solution of these salts be added, the passage of a current of carbonic or sulphurous anhydride through the solutions will determine their coagulability.

Sodium sulphate, and potassium acetate retard the coagulation. Glycerol prevents heat coagulation, but the passage of a current of carbonic anhydride through the solution will restore coagulability. The "colloïde aspartique" gives a violet reaction with copper sulphate and potash, a yellow with nickel sulphate and potash, and a red-brown with cobalt sulphate and potash. Each colloïd gives a well marked xanthoproteïc reaction, and each is precipitated by trichloracetic acid and by salicylsulphonic acid, the latter precipitate being coagulated on heating. This remarkable resemblance to proteïd is accentuated by the fact that intravascular injection into a rabbit of a few c.c. of a 1 per cent. solution causes complete intravascular coagulation. W. D. H.

Uroerythrin. By Archibald E. Garrod (*J. Physiol.*, 1895, **17**, 439—450).—The colouring matter of pink urate sediments has been termed uroerythrin, but its nature has never been satisfactorily determined. B. Mester's opinion that it is a scatole derivative is considered to be untenable. Reale's view (*Rivista Clin. e Terapeut.*, 1891) that it is urobilin has also been shown to be incorrect by Riva (*Gaz. med. di Torino*, 1892, **43**, 1 and 923) and Zoja (*Archiv. Ital. di Clin. Med.*, 1893, **32**, 63). The principal results of Riva and Zoja's work is as follows:—The sediment is washed upon the filter-paper with ice cold water, dried, and soaked in absolute alcohol; it is next dissolved in warm water, and extracted with amylic alcohol, which takes up all the uroerythrin, and after filtration is clear. Cold absolute alcohol dissolves isolated uroerythrin readily, but does not extract the pigment from urate sediments. The solutions have a ruddy orange tint; they absorb the blue end of the spectrum, but dilute solutions show two absorption bands united by shading between E and F. Strong sulphuric and hydrochloric acid impart a pink colour to the solutions, but acetic acid produces no immediate change. Caustic alkalis destroy the pigment and change its colour to green. Not unfrequently a play of colours is observed when an alkali is added; the green solution shows no absorption bands. Solutions of uroerythrin are rapidly decolorised by actinic light, which, however, has little effect on the solid pigment and none at all on pink urate sediments. The pigment is precipitated by salts of lead, barium, calcium, and tin, and the precipitate is pink. Solid uroerythrin leaves no ash on combustion, and gives off only a small quantity of ammonia when heated with caustic potash.

The present research shows that the colour of urate sediments varies, owing to the fact that other pigments take part in the coloration. These other pigments are urochrome, hæmatoporphyrin, bile pigments and chrysophanic acid (found in the urine of patients taking rhubarb, or senna).

In support of the hypothesis that the uroerythrin in urate sediments is in combination, it is found that the sediment constantly shows a definite absorption band on the blue side of the D line; the deposit is examined on filter-paper by reflected light, or the paper may be dried, oiled, and then examined by transmitted light. Uroerythrin itself in solid form or solution does not show this band.

The following new process for the extraction of uroerythrin from the sediment is described. The sediment is washed off a filter-paper by a stream of cold water, and gentle warmth applied until it dissolves. This solution is saturated with ammonium chloride, and the ammonium urate thus precipitated carries all the uroerythrin down with it; the filtrate generally shows a urobibin band. The precipitate is washed with a saturated solution of ammonium chloride until the washings have no longer a yellow tint; the filter-paper, with its deposit, is then soaked in warm alcohol for several hours in the dark, and on filtering, a more or less concentrated solution of uroerythrin is obtained. To this, twice its bulk of water is added, and the mixture is shaken with chloroform, which becomes yellow by removing impurities; this operation is repeated several times. Chloro-

form is then added together with a drop of acetic acid, when a chloroformic solution of uroerythrin is obtained. The chloroform is evaporated at a low temperature, and the solid residue dissolves readily in absolute alcohol. The quantity of pigment obtained even from deeply coloured solutions is very small. It leaves no ash, and contains no iron. The spectrum of the solution is that already given, and first accurately described by MacMunn. Its reactions are uncertain, as it is so rapidly bleached by light; strong sulphuric acid causes a brilliant carmine colour with a dark absorption band on the blue side of D; on exposure to light, it becomes greenish-yellow. If hydrochloric acid is used instead, a pink is obtained giving an ill-defined shading from λ608—517; it also becomes greenish on exposure to light. Phosphoric acid gives a salmon pink with two bands very like those of uroerythrin, but nearer the red; it is less rapidly decolorised by light than the original uroerythrin. In the case of all these acid products, the original colour and spectrum are restored by dilution with alcohol, and all are soluble in chloroform. Alkalis cause a play of colours, the final product being green. Acidification with acetic acid restores the uroerythrin, except after the green stage has been reached. The precipitation produced by metallic salts is considered to be due to precipitation of urates which carry down the pigment with them.

Clinical evidence points strongly to the liver as the probable seat of formation of uroerythrin, but no clue has as yet been obtained indicating a relation to, or derivation from the pigments of blood or bile. W. D. H.

Organic Chemistry.

Carbonyl Bromide and Chlorobromide. By J. Adolphe Besson (*Compt. rend.*, 1895, **120**, 190—192).—When a solution of aluminium bromide in carbonyl chloride is exposed to light, or heated at 100—150°, bromine and carbonic oxide are liberated. If, however, boron bromide is heated in sealed tubes at 150° for about 10 hours with half its weight of carbonyl chloride, almost the whole of the carbonyl chloride is decomposed, and the liquid remains colourless provided the temperature has not materially exceeded 150°. The product yields two fractions, 30—40° and 60—70°, containing a liquid which is only slowly attacked by water. If these fractions are added slowly to a solution of sodium thiosulphate cooled to 0°, and the oily liquids that separate are again distilled, they yield respectively carbonyl chlorobromide and carbonic bromide.

Carbonyl chlorobromide, $COClBr$, is a colourless liquid which expands rapidly when heated, and boils at 35—37°; sp. gr. at 0° = 1·98; vapour density 4·85 (Cal. 4·98).

Carbonyl bromide, $COBr_2$, is a yellowish liquid, expanding rapidly when heated, and boiling at 63—66°; sp. gr. at 0° = 2·48; vapour density 6·60 (Cal. 6·53).

Both liquids are gradually decomposed by water, and when distilled in contact with air they acquire a yellowish colour, owing to the liberation of bromine. When heated in sealed tubes at 100° with mercury, they are completely decomposed in a few hours. Their vapours are very irritating to the eyes and the respiratory organs.

C. H. B.

Action of Bromine on Ethers in Presence of Sulphur. By P. Genvresse (*Bull. Soc. Chim.*, 1894, [3], **11**, 888—891).—When bromine is added to a mixture of sulphur and ether, a brisk action takes place, ethylic and hydrogen bromides and water being evolved, the last probably from the action of the hydrogen bromide on the ether. The product contains dibromacetaldehyde, identical with that described by Hagemann (*Ber.*, 1870, **3**, 758). The *hydrate* (compare Pinner, *Annalen*, 1874, **173**, 67) forms colourless crystals, and melts at 63°; it is sparingly soluble in water, but freely in alcohol or ether. Its vapour pressure at ordinary temperatures is considerable, so that it readily dissociates in a dry atmosphere under low pressure; it is also decomposed by light. The vapour is irritating to the eyes.

Amylic ether, prepared by Friedel's method of heating the iodide with excess of the alcohol (10 parts) at 200°, is acted on more quickly than ethylic ether. The chief products are amylic bromide and *bromisovaleraldehyde;* the latter boils and decomposes slightly at 105° (25 mm.), and is stated to be identical with that obtained by Étard (Abstr., 1892, 809).

Jn. W.

Active Amylic Ethereal Salts and Ethers. By Philippe A. Guye and L. Chavanne (*Compt. rend.*, 1895, **120**, 452—454).—The

position of the maximum of $[\alpha]_D$ in the series of amylic salts of normal acids of the acetic series (this vol., i, 202) does not vary between 20° and 70°. The values are—

t.	Formate.	Acetate.	Propionate.	Butyrate.	Palmitate.
20—22°	+2·01	+2·53	+2·77	+2·69	+1·45
60—70	+1·98	+2·51	+2·68	+2·54	+1·16

Ethers derived from active amylic alcohol ($[\alpha]_D = -4·4$) gave the following results.

	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$.	Product of asymmetry.
Methylic amylic ether.	87·5—88·5°	0·754	+0·39	218
Ethylic amylic „ .	107·5—109	0·759	+0·61	332
Propylic amylic „ .	125·0—127	0·783	+0·90	374
Isobutylic amylic „ .	145·0—147	0·773	+0·96	373
Isoamylic amylic „ .	—	0·774	+0·70	351
Cetylic amylic „ .	—	0·805	+0·31	104
Benzylic amylic „ .	231·0—232	0·911	+1·83	(307)

Even if the isobutyl and isoamyl compounds are left out, the existence of a maximum in both rotatory power and product of asymmetry is obvious.

Ethereal salts of active secondary amylic alcohol prepared by Le Bel gave him the following results, which, however, must be accepted with some reserve.

	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$.	Product of asymmetry.
Secondary amylic acetate.....	125—130°	0·962	−4·06	249
„ „ propionate..	145—150	0·895	−8·55	390
„ „ butyrate....	165—170	0·889	−8·25	483
„ „ valerate....	—	—	—	490
„ „ caproate ...	—	—	—	487

All the series of compounds investigated show a maximum rotatory power practically coincident with that indicated by the product of asymmetry, but this maximum ought not to occur in all homologous series of active compounds. If in a series of active amylic ethereal salts, the first term should be derived from an acid of high molecular weight, this term will already be on the descending branch of the curve, and the rotatory power will constantly decrease in the series. This is the case with the series of ethereal salts derived from active primary amylic alcohol, the first term being the benzoate.

	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$.	Product of asymmetery.
Amylic benzoate	253—254°	0·988	+4·96	275
„ phenylacetate.....	265—266	0·982	+3·84	245
„ phenylpropionate.....	279–281	0·976	+2·15	218

C. H. B.

Action of Chlorine on Ethylenic Glycol. By LEON DONCIU (*Monatsh.*, 1895, **16**, 1—12).—The primary product of the interaction of chlorine and ethylenic glycol is the unstable compound

$$OH{\cdot}CHCl{\cdot}CHCl{\cdot}OH,$$

which readily changes into glyoxal. The hydrogen chloride formed during this first change reacts with a further quantity of glycol, producing glycol chlorhydrin, part of which distils over at the temperature of the action, and the remainder combines with more glycol to form polyethylene glycols. By the continued action of chlorine, these are converted into the corresponding aldehydes, and, with them, apparently constitute that portion of the product of the action of chlorine on ethylenic glycol which is insoluble in ether and only sparingly soluble in water. The derivative $C_2H_2(OH)_2Cl_2$ forms, with 2 mols. of glycol, a compound having the formula $C_6H_{11}ClO_4$, and this appears to be the chief part of the product of the action soluble in ether. A substance of the same formula can also be obtained by the interaction of glyoxal, glycol, and chlorhydrin in presence of hydrogen chloride. The compound $C_6H_{11}ClO_4$ may have the constitution

$$OH{\cdot}C_2H_4{\cdot}O{\cdot}CH<\begin{matrix}CHCl-\\O{\cdot}C_2H_4\end{matrix}>O \quad \text{or} \quad Cl{\cdot}C_2H_4{\cdot}O{\cdot}CH<\begin{matrix}CH(OH)\\O-C_2H_4\end{matrix}>O.$$

It is a yellow oil which, on treatment with sodium ethoxide, gives the compound $C_2H_4<\begin{matrix}O{\cdot}CH{\cdot}O\\|\\O{\cdot}CH{\cdot}O\end{matrix}>C_2H_4$. This melts at 134—135°, and can be synthetically prepared by the interaction of glyoxal and glycol in presence of hydrogen chloride. It appears to bear the same relation to its generators as ordinary acetal does to aldehyde and ethylic alcohol respectively. G. T. M.

Ethylenic Oxide. By ERNST ROITHNER (*Monatsh.*, 1894, **15**, 665—682).—The most suitable drying agent for ethylenic oxide is soda-lime, calcium chloride, as employed by Demole (*Annalen*, **173**, 125), being decomposed by the moist oxide with formation of lime and ethylene chlorhydrin. When added to a solution of iodine in potassium iodide, ethylenic oxide is converted into iodoform. With piperidene, it forms Ladenburg's hydroxyethylpiperidine,

$$C_5NH_{10}{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

which yields a hydrochloride melting at 120°. With pyridine, it gives only a resinous mass, but ethylene chlorhydrin and pyridine

yield the expected base, which is characterised by its forming a platinochloride, $(C_7NH_{10}OCl)_2PtCl_4$, melting at 175°. When a mixture of ethylenic oxide and phenylhydrazine, in molecular proportion, is heated in sealed tubes at 100°, a product is obtained, the chief portion of which boils at 180—187° (10 mm.), and corresponds nearly with the formula $N_2H_2Ph{\cdot}C_2H_4{\cdot}OH$. If, however, a large excess (4—5 mols.) of ethylenic oxide is employed, the oil $PhN_2H_3,5C_2H_4O$ is formed; this boils at 230—240° (10 mm.), and is resolved on treatment with fuming hydrobromic acid into ammonia and ethylenic dibromide. Ethylenic oxide and sodium ethoxide, when heated in sealed tubes at 100°, give a product which boils at 110—120° (25 mm.); this is resolved by hydriodic acid at 100° into ethylic and ethylenic iodides, and must therefore be regarded as a complex ethylic polyethylenic oxide. Ethylenic oxide and phenol, in molecular proportion, when heated in sealed tubes at 150° for 10 hours, yield the *monophenyl derivative of glycol*, $HO{\cdot}C_2H_4{\cdot}OPh$; this boils at 237°, and, when heated with acetic anhydride at 150°, forms a *monacetin*, $C_{10}H_{12}O_3$, boiling at 241—243°. If heated with hydrobromic acid or hydriodic acid, the monophenyl derivative is resolved into ethylenic bromide and phenol, and ethylic iodide and phenol respectively.

Ethylenic oxide readily polymerises when it is mixed with a little potash and gently heated at 50—60°. The product melts at 56°, and appears to have a very complex molecule, perhaps $(C_2H_4O)_{30}$, since it hardly affects the boiling point and the melting point when it is dissolved in benzene and in acetic acid respectively. It is completely converted into ethylic iodide when heated with hydriodic acid at 250°. G. T. M.

Action of Ammonia on *d*-Glucose. By WINTHROP E. STONE (*Amer. Chem. J.*, 1895, **17**, 191—196; compare Abstr., 1894, i, 221). —*d*-Glucose dissolves in absolute alcohol which has been saturated with ammonia, and the solution is precipitated by carbonic anhydride and by hydrochloric acid, mixtures of glucose and ammonium salts being formed. If the solution is kept in a closed vessel for several weeks, a white, crystalline *ammonia derivative*, $C_6H_{12}O_6,NH_3$, analogous to other aldehyde-ammonias, separates. This compound melts at 122—123° (uncorr.), and has a specific rotation in aqueous solution of $[\alpha]_D = +22—22{\cdot}7°$, no birotation being observed (compare the fact that small quantities of ammonia destroy the birotation observed in sugar solutions). The new ammonia derivative is stable at the ordinary temperature; the presence of the ammonia seems to protect the molecule from many reactions; thus, in solution, the compound is only very slowly fermented by yeast, and with difficulty yields a precipitate with phenylhydrazine; 5·7 milligrams are required in a 1 per cent. solution to reduce 1 c.c. of Fehling's solution (undiluted).

By the action of hydrogen sulphide on the ammoniacal alcohol solution of *d*-glucose, a crystalline compound is obtained which appears to be a thialdine, but has not been thoroughly investigated.

A. G. B.

Arabinochloral and Xylosochloral. By MAURICE HANRIOT (*Compt. rend.*, 1895, **120**, 153—155).—Arabinose and xylose do not readily combine with pure chloral, except in presence of a minute quantity of hydrochloric acid. Twenty-five parts of the sugar and 50 parts of anhydrous chloral, with a small quantity of hydrochloric acid, are heated at 100° for an hour, the product repeatedly distilled with water to remove unaltered chloral, and the aqueous solution filtered and concentrated.

Arabinose yields two isomeric substances of the composition $C_7H_9Cl_3O_5$, one of which is considerably more soluble in various solvents than the other. *β-Arabinochloral* forms small crystals or lamellæ, which melt and sublime at 183°. Under reduced pressure, it can be distilled without decomposing. It is only slightly soluble in water and chloroform in the cold, but dissolves somewhat readily in hot alcohol, benzene, or ether. Its rotatory power $[\alpha]_D = -23{\cdot}2°$. With various reagents, it behaves like glucochloral or chloralose (Abstr., 1893, i, 247, and 1894, i, 105), but gives a blue coloration instead of red with a hydrochloric acid solution of orcinol. The *triacetyl derivative* forms prisms, melts at 92°, and is insoluble in water, but readily soluble in alcohol, ether, and chloroform; it readily decomposes with liberation of acetic acid. *Dibenzoylarabinochloral* melts at 138°, and is only slightly soluble in ether, although very soluble in alcohol and chloroform. No tribenzoyl derivative is formed, even in presence of zinc chloride. When oxidised with permanganate, *β*-arabinochloral yields small quantities of an acid which seems to be isomeric with the chloralic acids previously described (*loc. cit.*).

α-Arabinochloral is contained in the mother liquor from the preceding compound, and is more soluble in all solvents; it crystallises in lamellæ which melt at 124°. The dibenzoyl derivative melts at 138°, and is very soluble in ether, alcohol, and chloroform. The acetyl derivative is insoluble in water, but soluble in organic solvents.

Xylosochloral is formed less readily under similar conditions, and requires more hydrochloric acid and longer heating. It crystallises from water in lamellæ which melt at 132°, and sublime partially below this temperature. Its rotatory power $[\alpha]_D = -13{\cdot}6°$, and it gives a blue coloration with orcinol in acid solution; it is much more soluble in water than arabinochloral. The acetyl derivative is unstable, and was not isolated. *Dibenzoylxylosochloral* forms small crystals insoluble in water.

The constitution of these derivatives is similar to that of glucochloral (*loc. cit.*), and it is probable that the anhydric oxygen is derived from two of the secondary hydroxyl groups, the tertiary hydroxyl remaining unaltered. C. H. B.

Acetates derived from Sugars. By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 194—197).—Experiments were made with a view to determine the influence of the presence of fused sodium acetate and zinc chloride respectively on the acetates obtained by the action of acetic anhydride on sugars. Stable sugars, such as inosite, yield the same products in either case. Saccharoses and polysaccharides in presence of sodium acetate yield salts from which the original carbo-

hydrates can be obtained by the action of alkalis, and the molecular weights of which, as determined by cryometric methods, agree with the formulæ. On the other hand, in presence of very small quantities of zinc chloride, the acetates obtained are those of the glucoses derived from the saccharoses and polysaccharides by hydrolysis.

With glucoses, the reaction is more complex. From ordinary dextrose, three *pentacetins*, α, β, and γ, can be obtained under different conditions. The *α-pentacetin* is obtained when very small quantities of zinc chloride or somewhat larger quantities of sodium acetate are used; it forms silky needles which melt at 130°; dextrorotatory power in 9 per cent. solution in chloroform or benzene $[\alpha]_D = +4°$. At 15°, it dissolves in 76 parts of alcohol of 95°, 47 parts of ether, and 7 of benzene, and is slightly soluble in water, and soluble in all proportions in chloroform. The *β-pentacetin* constitutes about 20 per cent. of the product when a large quantity of sodium acetate is used, and is almost the sole product with a moderate quantity of zinc chloride. It melts at 82°, and its dextrorotatory power in a 9 per cent. solution in chloroform is $[\alpha]_D = +59°$. It is more soluble in all the solvents than the α-derivative. The *γ-pentacetin* is obtained by boiling either of the preceding compounds with 5 per cent. of zinc chloride, and twice their weight of acetic anhydride. It forms needles which melt at 111°; dextrorotatory power $[\alpha]_D = +101{\cdot}75°$; solubility in alcohol and ether intermediate between that of the α- and β-compounds, but extremely soluble in chloroform and benzene. C. H. B.

Araban. By F. Ullik (*Chem. Centr.*, 1894, ii, 31—32; from *Öster. Z. Zucker-Ind. u. Landw.*, 1894, **23**, 268—275).—*Araban*, $C_5H_8O_4$, is a compound which possesses the properties characteristic of an anhydride of arabinose, and has been isolated from the pulp of the sugar-beet and from other beet-root products. It is a white, amorphous substance, insoluble in alcohol, but soluble in water. The aqueous solution does not reduce Fehling's solution, nor does it give precipitates with the hydroxides of the alkali and alkaline earth metals, nor with normal and basic lead acetates; hence the behaviour of the compound resembles that of dextrin. Araban shows Tollens' reaction with phloroglucinol and hydrochloric acid, and is optically active, $[\alpha]_D = -83{\cdot}9$; dilute acids easily convert it into arabinose. Treatment with strong sulphuric acid converts arabinose into a substance which completely resembles araban in most of its properties, but has a rotation of $[\alpha]_D = +242{\cdot}1$; this rotation, however, is dependent on the temperature of treatment, just as, according to Hönig and Schubert, is the case with the rotation of dextrin.

A. G. B.

Blue Iodine Compounds of Starch and Cholic acid. By Fritz W. Küster (*Ber.*, 1895, **28**, 783—785; compare this vol., i, 199).—The author insists, in opposition to Mylius (this vol., i, 313), that the blue "compound" of iodine with starch is really a solid solution of iodine in starch; were it a compound, it would give, by dissociation in contact with potassium iodide solution, a solution in which the concentration of the iodine would be constant, whereas, in fact, this concentration alters with that of the solid. Cholic acid,

however, forms a true compound with iodine, for in this case the concentration of the iodine in the contiguous potassium iodine solution is actually constant. C. F. B.

Chitin and the Cell Membrane of Fungi. By EUGEN GILSON (*Ber.*, 1895, **28**, 821—822).—The author claims priority over Winterstein (this vol., i, 80) and Hoppe-Seyler (this vol., i, 166) with regard to the discovery of the fact that the characteristic reactions of chitin are also given by the cell-membrane of many species of fungus. **A. H.**

Two Carbohydrates from Fungi. By ERNST WINTERSTEIN (*Ber.*, 1895, **28**, 774—777).—The carbohydrates are extracted from the fungus by digestion with cold 6 per cent. aqueous soda, the proteids having been first removed by treatment with very dilute ammonia; they are then precipitated from the alkaline solution by the addition of acids or salts. Both are white, amorphous substances and greatly resemble the paradextran obtained from *Boletus edulis* (Abstr., 1894, i, 161); they yield *d*-glucose when hydrolysed.

Paraisodextran, $C_6H_{10}O_5$, from *Polyporus betulinus*, does not reduce Fehling's solution, and is optically active, having a specific rotation $[\alpha]_D = +240°$ in a 4 per cent. solution in 5 per cent. soda; it is coloured blue by strong sulphuric acid and iodine. *Pachymose* (C 41·07, H 7·07 per cent.), from *Pachyma cocos*, originally prepared by Champignon, is coloured yellow by iodine and sulphuric acid; optical activity could not be detected in it. C. F. B.

Action of Nitric acid on Lignocelluloses. By EDWARD C. C. BALY and JOHN C. CHORLEY (*Ber.*, 1895, **28**, 922—927).—The chief object of this investigation was the determination of the gaseous products formed by the oxidation of wood with nitric acid. Box-wood was treated with 33 per cent. of nitric acid (10 per cent. solution), during 4—5 hours, and the action completed by heating on the water bath. In one experiment, 9 grams of wood, dried at 100°, and 35 grams of nitric acid (9·64 per cent.) yielded 1156 c.c. of gas consisting of N_2 = 18·3; N_2O = 9·4; NO = 9·3; NO_2 = 33·2; HCN = 8·3; CO_2 = 17·2; CO = 4·3 per cent. This shows that the amount of nitric acid completely reduced, to N_2 or N_2O, corresponds with only 20 per cent. of the wood employed, and that only 2·95 per cent. of the carbon of the wood is converted into gaseous substances. The remaining products of the oxidation consisted of: fibrous residue = 48·00; volatile acids = 11·80; oxalic acid = 3·84; soluble derivatives of the non-celluloses = 26·16 per cent. The fibrous residue was almost pure cellulose; the volatile acids are calculated as acetic acid, and consisted chiefly of this; the proportion varies according to the material employed, with jute it is similar to box-wood, with pine only 3—4 per cent. is formed. The soluble substances are strongly acid, and no definite compound could be isolated. When further oxidised, oxalic acid, oxides of carbon, and volatile acids are formed; when fused with alkali, carbonic anhydride, oxalic acid, and acetic acid are produced. The reaction consists essentially in the destructive oxidation of a keto-R-hexene

group of the "non-cellulose" complex, whilst the pentosans, which are simultaneously formed, dissolve. J. B. T.

Isoundecylamine. By GIACOMO PONZIO (*Gazzetta*, 1894, **24**, ii, 277—288).—*Isoundecylamine*, $NH_2{\cdot}CHMe{\cdot}C_9H_{19}$, prepared by reducing methylnonylketoxime with sodium amalgam in acetic acid solution, is a colourless, hygroscopic liquid, lighter than and insoluble in water; it boils at 230—231° under 741 mm. pressure, has an alkaline reaction, readily absorbs carbonic anhydride, and soon changes to a white, solid mass on exposure to air. Its *hydrochloride*, $C_{11}H_{23}{\cdot}NH_2,HCl$, which crystallises in flat needles melting at 83—84°, is soluble in ether or light petroleum, and, with mercuric chloride, forms a white *compound*, $(C_{11}H_{25}N,HCl)_2HgCl_2$?, soluble in alcohol. The *platinochloride* crystallises in lustrous, yellow laminæ which blacken at 240°. The *acetyl*, $C_{11}H_{23}{\cdot}NHAc$, and *benzoyl*, $C_{11}H_{23}{\cdot}NHBz$, derivatives, prepared in the ordinary way, crystallise in thin needles melting at 58° and 84° respectively. The *benzylidene* derivative, $C_{11}H_{23}{\cdot}N{:}CHPh$, is prepared by the aid of benzaldehyde; it is a colourless liquid, boiling at 197—198° under 17 mm. pressure, but decomposing at 240° under atmospheric pressure.

Isoundecylammonium isoundecyldithiocarbamate,

$$C_{11}H_{23}{\cdot}NH{\cdot}CS{\cdot}S{\cdot}NH_3{\cdot}C_{11}H_{23},$$

prepared by the action of carbon bisulphide on isoundecylamine in ethereal solution, crystallises in small, white prisms melting at 66°. On heating with alcohol, it yields *α-diisoundecylthiocarbamide*, $CS(NH{\cdot}C_{11}H_{23})_2$, which crystallises in lustrous laminæ melting at 50—51°; on treating this with potassium platinosochloride in alcoholic solution, *platosodiisoundecylthiocarbamide*, $4CS(NH{\cdot}C_{11}H_{23})_2,PtCl_2$, is obtained as a yellow powder melting at 60°.

α-Diisoundecylcarbamide, $CO(NH{\cdot}C_{11}H_{23})_2$, is obtained by the action of yellow mercuric oxide on the corresponding thio-compound; it crystallises in lustrous, flat needles melting at 94—95°.

Isoundecylthiocarbimide, $C_{11}H_{23}{\cdot}N{:}CS$, is obtained together with isoundecylamine hydrochloride by distilling isoundecylammonium isoundecyldithiocarbamate with mercuric chloride and water; it is a colourless liquid, possessing but a slight odour of mustard oil, and boils at 163—164° under 17 mm. pressure, but decomposes slightly at 270° under atmospheric pressure. On treatment with alcoholic ammonia, it yields *monisoundecylthiocarbamide*, $C_{11}H_{23}{\cdot}NH{\cdot}CS{\cdot}NH_2$, which crystallises in lustrous tablets melting at 95°; the *platoso*-derivative is obtained in yellow crusts melting at 200°.

Monisoundecylcarbamide, $C_{11}H_{23}{\cdot}CO{\cdot}NH_2$, prepared by the action of yellow mercuric oxide on the corresponding thio-compound, crystallises in lustrous laminæ melting at 127°.

Isoundecylphenylthiosemicarbazide, $C_{11}H_{23}{\cdot}NH{\cdot}C(SH){:}N{\cdot}NHPh$, is obtained in two stereoisomeric forms by the action of phenylhydrazine on isoundecylthiocarbamide; the α- or labile modification melts at 80—100°, and changes on heating into the stable β-form, which crystallises in lustrous laminæ melting sharply at 109°. W. J. P.

Action of Formaldehyde on Hydroxylamine and Methylamine Hydrochlorides. By ANDRÉ BROCHET and R. CAMBIER (*Compt. rend.*, 1895, **120**, 449—452).—When excess of formaldehyde is added to a solution of hydroxylamine hydrochloride, the whole of the hydrochloric acid is liberated; if, on the other hand, the hydrochloride is in excess, the quantity of acid liberated is strictly proportional to the quantity of aldehyde added, and, by titrating with methyl-orange as indicator, the aldehyde can then be accurately estimated.

If a solution containing formaldehyde and any salt of hydroxylamine, whether acid or alkaline, is boiled, hydrocyanic acid is formed, and this is a delicate and characteristic reaction for formaldehyde, since other aldehydes yield nitriles.

When formaldehyde and methylamine hydrochloride are mixed in solution, the liquid remains neutral to methyl-orange, and becomes acid to phenolphthalein, owing to the formation of a weak base, which separates as an upper layer on adding excess of solid potash. This base, which boils at 166°, was first obtained by L. Henry (*Bull. Acad. Sci. Belge*, [3], **26**, 200), who found its vapour density to be 1·52, and regarded it as the compound $NMe:CH_2$. It seemed unlikely, however, that a compound of this constitution should boil at so high a temperature, and the authors find that it is really *trimethyltrimethylenetriamine*, its vapour density being 1·81 (Cal. 1·49), and its molecular weight by the cryometric method in benzene 122·75 (Cal. 129). It yields very soluble salts, which do not crystallise from water or alcohol, but the hydrochloride can be obtained in crystals by the action of dry hydrogen chloride on a solution of the base in benzene. C. H. B.

Action of Formaldehyde on Methylamine and Ammonia. By PAUL DUDEN and MAX SCHARFF (*Ber.*, 1895, **28**, 936—939).—The mechanism of the formation of hexamethylenetetramine has not yet been ascertained, although in all probability a simple condensation occurs in the first instance similar to that which takes place between formaldehyde and the primary amines. The relatively stable, feeble bases thus formed, of which methylenemethylamine is a type, are considered by L. Henry to be represented by the formula $CH_2:NR$, but Brochet and Cambier (preceding abstract), from observations of vapour density, find that this formula must be tripled, a view confirmed by v. Miller and Plöchl's investigation of anhydroformaldehydeaniline, which undoubtedly has the formula $(CH_2:NPh)_3$.

To decide the question of the molecular weight of methylenemethylamine from a purely chemical standpoint, the authors have prepared the picrate, and find that its formula is $(CH_2:NMe)_3,C_6H_6N_3O_7$, thus confirming Brochet and Cambier's conclusions. *Trimethyltrimethylenetriamine picrate*, from the perfectly dry base and acid in ethereal solution, crystallises in large prisms, and melts at 127—128°; it is soluble in water, by which it is hydrolysed, on boiling, into formaldehyde and methylamine picrate.

Attempts to prepare a similar picrate from the product of the action of formaldehyde on aqueous ammonia were unsuccessful, nor

could a definite platinochloride or aurochloride be obtained. On adding benzoic chloride, however, to the product in presence of excess of caustic soda, *tribenzoyltrimethylenetriamine*, $(CH_2{\cdot}NBz)_3$, was obtained as a sticky, curdy mass, which, after purification, crystallised from ether-chloroform in small, well-defined, colourless octahedra, and melted at 220—221°; its molecular weight was determined by the cryoscopic method. It was accompanied by a small quantity of a substance melting at 202—204°. Tribenzoyltrimethylenetriamine is hydrolysed by mineral acids into benzoic acid, formaldehyde, and ammonia, but although in this respect as well as in melting point it resembles methylenedibenzamide (*Annalen*, 1884, **223**, 47), it is not identical with that substance, as its crystallographic constants and solubilities are quite different.

The authors consider that the probable constitution of these methyleneamines is $NR<^{CH_2{\cdot}NR}_{CH_2{\cdot}NR}>CH_2$. Jn. W.

Action of Formaldehyde on Ammonium Salts. By André Brochet and R. Cambier (*Compt. rend.*, 1895, **120**, 557—560).—When formaldehyde is mixed with ammonium chloride, trimethylenetriamine hydrochloride is probably formed (this vol., i, 325) with liberation of hydrochloric acid, but the latter tends to reverse the action, and hence a condition of equilibrium is set up varying with the temperature, &c. If the acid is neutralised, by means of chalk or otherwise, as fast as it is formed, hexamethylenetetramine is obtained, but, if the proportion of acid is increased sufficiently, the products are completely reconverted into ammonium chloride and formaldehyde. It would seem that one or more bases exist intermediate between ammonium and hexamethylenetetramine. The proportion of nitrogen in the platinochlorides obtained from the solution increases with the proportion of hydrochloric acid present, and nitrous acid yields nitroso-derivatives of pentamethylenetetramine and trimethylenetriamine.

If a solution of formaldehyde and ammonium chloride is heated, the former, whether present in excess or not, acts on the trimethylenetriamine first formed, and yields methylamine in calculated quantity, $2(CHNH_2Cl)_3 + 3CH_2O + 3H_2O = 6NH_2Me,HCl + 3CO_2$ (compare Delépine, following abstract). If the ammonium chloride is in large excess, the amine is very pure; if the aldehyde is in large excess, trimethylamine is the final product.

The formation of trimethylamine from ammonium salts and excess of formaldehyde has been observed by Plöchl (Abstr., 1888, 1051). Other ammonium salts behave similarly, hexamethylenetetramine being the sole product if the liquid is kept neutral. In hot solutions, methylamines are formed together with some methylal produced by the action of the aldehyde on the methylic alcohol, which is usually present as an impurity. C. H. B.

Hexamethylenetetramine. By Marcel Delépine (*Compt. rend.*, 1895, **120**, 197—199; 501—502).—Hexamethylenetetramine can be obtained by the action of a solution of ammonia in methylic alcohol

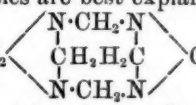
on methylenic chloride and chlorobromide. Cryometric determinations in acetic acid solution freshly prepared indicate a molecular weight of 137 (Cal. 140), but the value decreases with the time, in consequence of partial decomposition of the amine, which can be readily detected by means of Nessler's reagent, on which the amine itself has no action. The platinochloride has the composition $C_6H_{12}N_4,H_2PtCl_6 + 4H_2O$.

Inorganic acids convert the amine into ammonia and the aldehyde. Methylic and ethylic iodides yield derivatives of the type $C_6H_{12}N_4RI$, as Vohle has stated, and the author finds that they have the properties of quaternary ammonium iodides, and hence hexamethylenetetramine is a tertiary base.

Griess described a nitroso-derivative, dinitrosopentamethylenetetramine, $(CH_2)_5(NO)_2N_4$, which yields nitrogen, ammonia, and formaldehyde when heated with dilute hydrochloric acid. With cold acetic acid, however, the reaction is $2(CH_2)_5(NO)_2N_4 = (CH_2)_6N_4 + 4N_2 + 4CH_2O$, the same quantity of nitrogen being liberated, but the residues $(CH_2)_3N_2$ combining to form the original amine instead of undergoing hydrolysis. Mayer described another nitroso-derivative, $(CH_2{\cdot}N{\cdot}NO)_n$, and he adopted 3 as the value of n. The author, however, considers that the compound is $(CH_2)_4(NO)_4N_4$, and, as a matter of fact, the compound has no basic properties, whereas Griess's compound is dibasic.

With nascent hydrogen, hexamethylenetetramine yields trimethylamine and ammonia.

These properties are best explained by ascribing to the amine the constitution



Hexamethylenetetramine amyliodide forms white, nacreous lamellæ, which soften at 146°, and melt at about 156°; it combines with three atomic proportions of iodine to form a deep green, crystalline compound, which melts at 127°.

When the hexamethylenetetramine alkyliodides are boiled with dilute hydrochloric acid, they are hydrolysed in accordance with the equation $C_6H_{12}N_4RI + 6H_2O = 6CH_2O + 3NH_3 + NRH_3I$. This reaction affords a new method for the preparation of primary amines. Bismuth iodide is a valuable reagent for the separation of the amines from ammonia, and in the case of amylamine it indicates the presence of a secondary product which is at present under investigation.

C. H. B.

Triacetonamine. By Icilio Guareschi (*Chem. Centr.*, 1894, ii, 197—198; from *Atti. Accad. Sci. Torino*, **29**).—Mesityl oxide is converted into diacetonamine by the action of ammonia, similarly *triacetonamine* is produced by the action of ammonia on phorone, even in the cold. It forms large, colourless crystals melting at 34·9°, when moist at 39·6°; the *platinochloride*, $(C_9H_{17}NO)_2,H_2PtCl_6$, may be crystallised with $3H_2O$; the *platinothiocyanate* is a lemon-yellow salt. By employing amines instead of ammonia in the above reaction, alkyl derivatives of triacetonamine are obtained. *Methyltriacetonamine*,

$C_9H_{16}MeNO$, is a yellow, alkaline oil of unpleasant odour, forming a crystalline *platinochloride*, *platinothiocyanate*, *chloride*, *aurochloride*, and *picrate*. *Ethyltriacetonamine* is also a yellowish, strongly-alkaline oil, from which many salts have been prepared. *Allyltriacetonamine*, $C_3H_5 \cdot C_9H_{16}NO$, cannot be obtained quite pure, as it is readily resolved into allylamine and phorone, but the author obtained a crystalline *platinochloride*.

In the reaction with benzylamine and phorone, another base is produced as well as *benzyltriacetonamine*, $C_9H_{16}(C_7H_7)NO$; the former will be described in a future communication, the latter is a colourless, alkaline liquid, resembling in odour triacetonamine and trimethylamine; it cannot be crystallised, but has yielded many salts.

D. A. L.

Action of Ethylenediamine on Phorone and Mesityl Oxide. By Icilio Guareschi (*Chem. Centr.*, 1894, ii, 198; from *Atti Accad. Sci. Torino*, **29**).—Pulverised phorone, mixed with ethylenediamine hydrate dissolved in water, yields acetone and a base, $C_8H_{16}N_2$, which has not been named, but is also produced by the action of ethylenediamine on mesityl oxide. It is an oily liquid with pungent odour, and appears to crystallise after prolonged exposure over sulphuric acid; the *platinochloride*, $C_8H_{16}N_2,H_2PtCl_6$, and the *platinothiocyanate* have been prepared. It decomposes into ethylenediamine and acetone when distilled with water. D. A. L.

Action of Nitrous acid on Amidouracil and Amidoacetone. By Angelo Angeli (*Gazzetta*, 1894, **24**, ii, 366—371).—The author has previously suggested (*Gazzetta*, **23**, ii, 442) that the peculiar behaviour of the amidogen group in amidomethyluracil is due to the presence of the group $\cdot CO \cdot \underset{\|}{C} \cdot NH_2$; it is now shown that amidouracil itself can be converted into the diazo-compound which Behrend and Ernert (Abstr., 1890, 1240) prepared from amidouracilcarboxylic acid.

Amidoacetone also yields a *diazo-compound*; it was, however, only obtained in an impure state as a yellow oil, which effervesces with hydrochloric acid and yields bromacetone with hydrobromic acid. It is probably diazoacetylmethane, $CHAc<\overset{N}{\underset{N}{\|}}$. No diazo-compound could be prepared from diamidoacetone. W. J. P.

Diazomethane. By Hans v. Pechmann (*Ber.*, 1895, **28**, 855—861; compare Abstr., 1894, i, 438).—Diazomethane may be prepared by the action of aqueous or alcoholic alkalis on nitroso-acidyl derivatives of methylamine, especially on nitrosomethylurethane. This compound is best prepared by leading nitrous gases into urethane diluted with its own volume of ether. It is dangerous on account of its powerfully irritating action on the skin, lungs, and eyes; in these properties it resembles diazomethane. To prepare diazomethane, 1—5 c.c. of the above compound is mixed with an excess of dry ether and heated with excess of potash dissolved in methylic alcohol. About 50 per cent. of the theoretical yield of diazomethane is found

in the distillate. At ordinary temperatures it is a gas, but may be condensed to a dark yellow liquid, which boils at about 0°. Both organic and inorganic acids are converted into their methylic salts when treated with diazomethane in the cold. Alcohol is not acted on at ordinary temperatures, but phenol is slowly converted into anisoïl, and picric acid into trinitranisoïl. Bases react with diazomethane just as they do with ethylic diazoacetate; thus, paratoluidine gives methylparatoluidine.

The author suggests the use of diazomethane as a reagent for the preparation of the methylic derivatives of acids, phenols, and similar compounds in those cases in which the methylic derivatives cannot be readily obtained by other methods. As examples are given dimethylic phenylhydrazonemesoxalate, methylphthalimide, and β-methylumbelliferone methylic ether. When diazomethane is reduced with sodium amalgam and alcohol, the main product is methylhydrazine.

Diazomethane reacts with quinone, nitrosophenol, and nitrosomethylaniline, forming yellow or red compounds, which are being subjected to further examination. It also, like ethylic diazoacetate, unites with many unsaturated compounds to form additive compounds, but others, for instance, ethylene, stilbene, acetylene, tolane, &c., are not acted on. J. J. S.

Elimination of Carbonic Oxide. By Wilhelm Wislicenus (*Ber.*, 1895, **28**, 811—814; compare Abstr., 1894, i, 323).—Elimination of carbonic oxide on heating only occurs quantitatively in the case of derivatives of ethylic oxalacetate which contain the group COOEt·CO·CH·COOEt, but the action does take place, more or less completely, with a very large number of ketonic substances, among which are ethylic phenylcyanopyruvate, ethylic acetophenoneoxalate, from which ethylic benzoylacetate may be thus advantageously prepared, acetophenoneoxalic acid, ethylic ketipate, oxalyldiacetone, oxalyldiacetophenone, and diphenylketipionitrile.

The sodium and copper compounds of the ethereal oxalacetates either do not decompose at all, or only very slowly, even at temperatures above 200°. A. H.

Cuprammonium Double Salts. By Theodore W. Richards and Andrew H. Whitridge (*Amer. Chem. J.*, 1895, **17**, 145—154; compare Abstr., 1894, i, 113).—*Cuprammonium formochloride*,

$$Cu(NH_3)_2Cl\cdot CHO_2,$$

is prepared by dissolving cupric formate in alcohol, adding ammonium chloride, and passing ammonia into the liquid until a slight excess is present. The salt separates in blue, prismatic crystals on evaporation.

Ammoniocuprammonium acetobromide, $Cu(NH_3)_3Br\cdot OAc + H_2O$, is prepared like the ammoniocuprammonium acetochloride (Abstr., 1894, i, 113), which it resembles, except that it is much less stable.

Cuprammonium propionobromide, $Cu(NH_3)_2Br\cdot C_3H_5O_2$, was prepared by dissolving ammonium propionate in absolute alcohol, passing dry ammonia into the solution, and then warming it with precipitated

cupric oxide; very blue, prismatic crystals were deposited on evaporation.

Cuprammonium lactobromide, $Cu(NH_3)_2Br\cdot C_3H_5O_3$, is formed when syrupy lactic acid and cupric bromide are dissolved in alcohol and the solution is saturated with ammonia. It forms light blue crystals, which have a faint tinge of purple, and are permanent in air but immediately decomposed by water.

Cuprammonium lactochloride, $Cu(NH_3)_2Cl\cdot C_3H_5O_3$, resembles the bromide, but is of lighter colour; it is similarly prepared.

Similar compounds containing butyric acid could not be obtained.

A. G. B.

Cuprammonium Double Salts. By THEODORE W. RICHARDS and GEORGE OENSLAGER (*Amer. Chem. J.*, 1895, **17**, 297—305; compare Abstr., 1894, i, 113).—Attempts to prepare cuprammonium-acetofluoride proved fruitless. The following new iodine compounds have been prepared and analysed.

1. *Ammoniocuprammonium acetoiodide*, $Cu(NH_3)_3I\cdot OAc$, which forms brilliant, deep blue, monoclinic plates. It is not very permanent in the air, and is at once decomposed by water and acids.

2. *Octocuprammonium iodide acetate*, $Cu_8(NH_3)_{16}I(OAc)_{15}$, large, deep blue crystals, obtained from the mother liquors of the above compound.

3. *Tetrammoniotricuprammonium iodide*, $Cu_3I_6(NH_3)_{10}$. The crystals are black, and possess a bronze lustre, which soon disappears. They are immediately decomposed by water.

4. *Ammonium dicupric acetate*, $NH_4Cu_2(OAc)_3 + H_2O$. This forms bluish-green crystals, which dissolve in water without undergoing decomposition.

5. Cuprammonium acetate, $Cu(NH_3)_2\cdot OAc$, and also

$$Cu(NH_3)_2\cdot OAc,2\tfrac{1}{2}H_2O.$$

These two compounds have been previously obtained by F. Foerster (Abstr., 1893, i, 131). These, and other compounds, are being further investigated.

J. J. S.

Action of Ethylic α-Bromopropionate on Alkali Nitrites. By GASTON LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], **11**, 886—888; compare Abstr., 1894, i, 114, and this vol., i, 169).—In preparing the nitrosopropionates by this method, 2 mols. of sodium nitrite are necessary; probably the nitro-compound is formed in the first instance, and subsequently reduced by a second molecule of the nitrite. In confirmation of this view, when potassium nitrite is substituted for the sodium salt, potassium nitrate may be separated from the product.

An oily bye-product, $C_{10}H_{16}N_2O_7$, obtained in preparing ethylic nitrosopropionate, was probably *ethylic dinitrosolactate*, corresponding with the methylic salt previously described.

JN. W.

Alkylic Nitrosobutyrates. By GASTON LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], **11**, 883—886).—*Methylic α-nitrosobutyrate* forms a

brilliant, white mass, and melts at 61°. Like the nitrosopropionate, it is easily soluble in dilute alkalis, so that the molecule probably contains a :C:NOH group. The *silver* salt was prepared. The *ethylic salt* resembles the methylic salt, and melts at 51°.

On attempting to prepare ethylic nitrosoisobutyrate, the nitrosopropionate was obtained. JN. W.

Daturic acid. By ERNEST GÉRARD (*Compt. rend.*, 1895, **120**, 565—567).—A summary of those properties of daturic acid and its derivatives (Abstr., 1890, 1395, and 1892, 582), which prove that this acid is a distinct chemical individual and not a mixture of palmitic and stearic acids. C. H. B.

Substituted Ethereal Salts of Glycollic acid (Glycolylhydrazine). By THEODOR CURTIUS and NICOLAUS SCHWAN (*J. pr. Chem.*, 1895, [2], **51**, 353—371).—Ethylic glycollate may be prepared by adding the calculated quantity of water to a solution of ethylic diazoacetate (30 grams) in ether (100 grams), and dropping in 2 drops of sulphuric acid (1 : 5), the liquid being rapidly stirred the while. When the evolution of nitrogen has subsided, 4 grams of water and 14 drops of the acid are gradually added, excess of water is removed by calcium chloride, and the ethereal solution fractionated.

Ethylic benzylglycollate, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}COOEt$, is obtained when ethylic diazoacetate (5 grams) and benzylic alcohol (4·75 grams) are heated together until the evolution of nitrogen has ceased; it distils at 153—154° (12 mm.), and is a clear, colourless liquid, which becomes yellow after a time.

It was found that pure ethylic diazoacetate cannot be made to react with absolute alcohol, notwithstanding that the impure salt forms ethylic ethylglycollate under these conditions (compare *J. pr. Chem.*, 1888, [2], **38**, 424). Ethylic benzoylglycollate has been described before (*loc. cit.*). Ethylic hippurylglycollate (*loc. cit.*) may be prepared from ethylic diazoacetate and hippuric acid; the corresponding acid appears to be very unstable, attempts to hydrolyse the ethylic salt resulting in the production of ethylic hippurate.

Ethylic oxalylglycollate, $C_2O_2(O{\cdot}CH_2{\cdot}COOEt)_2$, is prepared by gradually adding 3·15 grams of anhydrous oxalic acid to 8 grams of ethylic diazoacetate, care being taken that the temperature does not rise; 2—4 grams of ethylic diazoacetate are next added, and when no more nitrogen is evolved the vessel is warmed until the liquid becomes clear; the crystals which separate on cooling are washed with ether, dissolved in that menstruum, the solution washed with alkali, dried by calcium chloride, and evaporated. Ethylic oxalylglycollate crystallises in slender, white needles, softens at 54°, melts at 58°, and dissolves sparingly in cold ether, more freely in alcohol, but not in water. *Ethylic succinylglycollate*, $C_2H_4(COO{\cdot}CH_2{\cdot}COOEt)_2$, is prepared in a similar manner; it forms long, colourless needles or laminæ, melts at 72·5°, and dissolves in hot ether and alcohol.

Hydrazine hydrate reacts with ethylic hippurylglycollate to form hippurylhydrazine (Abstr., 1891, 56) and glycolylhydrazine; with ethylic oxalylglycollate to form oxalylhydrazine (this vol., i, 264) and

glycolylhydrazine; and with ethylic succinylglycollate to form succinylhydrazine (*loc. cit.*) and glycolylhydrazine. Ethylic benzylglycollate and hydrazine hydrate react to form *benzylglycolylhydrazine*, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, which yields *benzylidenebenzylglycolylhydrazine*, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, when shaken with benzaldehyde; the last-named compound melts at 95°, and is freely soluble in hot, absolute alcohol.

The properties of *glycolylhydrazine*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, have been already described as those of amidoglycocine (hydrazineacetic acid, Abstr., 1891, 56). The compound is best prepared from ethylic oxalylglycollate, as indicated above, the oxalylhydrazine crystallising first; it yields the *hydrochlorides*, $C_2H_6O_2N_2,HCl$ (in aqueous solution), and $C_2H_6O_2N_2,2HCl$ (in alcoholic solution); the latter melts at 145—160°. With sodium ethoxide, it yields the compound $C_2H_6O_2N_2 + EtONa$.

Benzylideneglycolylhydrazine has been described as benzylidenehydrazineacetic acid (*loc. cit.*). *Orthohydroxybenzylideneglycolylhydrazine*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$, crystallises in yellowish-white, felted needles, and melts at 220—221°; the *para*-compound melts at 215—216°. *Acetophenoneglycolylhydrazine*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMePh$, obtained by heating acetophenone with the hydrazine at 130°, forms yellowish-white needles. *Ethylic glycolylhydrazineacetoacetate*,

$$OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt,$$

forms bitter crystals, melts at 112°, and dissolves freely in absolute alcohol, benzene, and ether.

Glycolylhydrazine anhydride (*hydraziglycolide*), $\begin{matrix}CH_2{\cdot}NH{\cdot}NH{\cdot}CO\\ |\\ CO{\cdot}NH{\cdot}NH{\cdot}CH_2\end{matrix}$, is obtained when glycolylhydrazine is heated for 10 hours in an oil bath at 170—175°, and the product recrystallised from alcohol; it crystallises in slender needles or laminæ, melts at 205—206°, and dissolves easily in water at 20°, but hardly at all in water at 0°; hot alcohol dissolves it, but not ether or benzene. It is decomposed when sublimed; its aqueous solution is neutral, and it behaves as a feeble base dissolving in acids. Caustic alkalis also dissolve it. It is stable towards hot dilute acids and alkalis, and exhibits indifference towards mercuric and silver salts. Its *hydrochloride*, $C_4H_8O_2N_4,HCl + H_2O$, melts at 40—42°, and is very soluble in water. The formation of this basic anhydride shows that the parent substance is glycolylhydrazine, and not hydrazineacetic acid, as formerly supposed (*loc. cit.*); another argument for the present view is, that when hydrogen chloride is passed into the hot alcoholic solution of glycolylhydrazine no etherification occurs, as would inevitably be the case were the compound hydrazineacetic acid. A. G. B.

Methylenic Lactate. By Louis Henry (*Compt. rend.*, 1895, **120**, 333—335).—When a mixture of paraformaldehyde with lactic acid in molecular proportion is heated for some time, it yields methylenic lactate, $CH_2<\begin{matrix}O{\cdot}CO\\ |\\ O{\cdot}CHMe\end{matrix}$, a colourless, mobile liquid, with a strong odour, and an extremely piquant taste. It boils at 153—154° under a

pressure of 754 mm.; sp. gr. at 2·5 = 1·1974; vapour density 5·47 (Cal. 3·52); it solidifies in a mixture of ether and solid carbonic anhydride, and melts at −28°. It is insoluble in water, and when heated with it yields lactic acid and formaldehyde, and the liquid has a strong reducing action on silver nitrate. Bromine dissolves it without appreciable effect; it combines explosively with the corresponding propylene derivative, and ammonia and primary and secondary alkylamines decompose it rapidly.

Trioxymethylene and glycerol, or its monochlorhydrin, yield respectively the compounds $\begin{matrix}OH\cdot CH_2\cdot CH-O\\ \quad\quad\quad\quad\ |\\ \quad\quad\quad CH_2\cdot O\end{matrix}>CH_2$, boiling at 197°, and $\begin{matrix}CH_2Cl\cdot CH-O\\ \quad\quad\quad\quad\ |\\ \quad\quad\quad CH_2\cdot O\end{matrix}>CH_2$, boiling at 150°.

C. H. B.

Rotatory Powers of Amylic Pyruvate and Lactate. By Louis Simon (*Bull. Soc. Chim.*, 1894, [3], **11**, 760—767).—*Active amylic pyruvate*, prepared by the direct action of the acid on the alcohol, is a limpid, colourless liquid, having a pleasant but peculiar odour. It boils at 185—186°, or at 85—86° (16 mm.). The sp. gr. = 0·984 at 15°. The specific rotatory power, $[\alpha]_D = +3·25°$ at 15°, and is practically the same in acetic acid solution, but rather lower (+3·12° to +3·21°) in ethylic acetate solution. The refractive index, $[\mu]_D = 1·420617$ at 19°, $[\mu]_\infty = 1·409170$; the temperature coefficient = −0·000474; the molecular refraction = 65·73, the calculated number being 66·23. *Active amylic lactate*, prepared in the same way from the active alcohol ($[\alpha]_D = −4·15°$) and inactive lactic acid, could not be separated into two optical isomerides, the acid obtained by hydrolysis of various portions being invariably inactive. It boils at about 195°, or at 94—95° (14 mm.), or 92° (11 mm.). The specific rotatory power, $[\alpha]_D = +2·5°$.

The relation between the specific rotatory powers of these salts is directly opposed to that required by Guye's law. As a similar deviation is shown by the similarly related compounds, *d*-fructose, *d*-mannose, and *d*-mannitol, it must be assumed that the moment of a ketonic or aldehydic chain is greater than that of the corresponding alcoholic chain.

Jn. W.

Optical Isomerides of α-Hydroxybutyric acid. By Philippe A. Guye and Charles Jordan (*Compt. rend.*, 1895, **120**, 562—565).—Quinine, strychnine, and brucine α-hydroxybutyrates crystallise well, but the cinchonine salt does not crystallise readily. By fractional crystallisation of these salts, the acid can be separated into its optically isomeric constituents, the best results being obtained with the brucine compound. The salt of the lævogyrate acid is less soluble than that of the dextrogyrate; after separation of the crystals, they are decomposed with ammonia. The first fractions are lævogyrate, but the rotatory power of successive fractions diminishes, and after a time the sign of rotation changes. The specific rotatory power of lævogyrate ammonium α-hydroxybutyrate $[\alpha]_D = −13·9$; for the isobutylic α-hydroxybutyrate $[\alpha]_D = −7·7$. This ethereal salt

boils at 190—200°; sp. gr. at 15° = 0·919. The ethereal salts of the lævogyrate acid are also lævogyrate, and are under investigation.

C. H. B.

Behaviour of Calcium Ethylglycollate on Dry Distillation. By WILHELM H. GINTL (*Monatsh.*, 1894, **15**, 803—806).—On dry distillation, calcium ethylglycollate (compare Heintz, *Jahresber.*, 1861, 448) yields a mixture of alcohol and *diethoxyacetone*, $CO(CH_2{\cdot}OEt)_2$; the latter boils at 189—194°, is soluble in water, and has a sweet but burning taste. In its mode of decomposition, the salt therefore behaves differently from the calcium salts of alkyl derivatives of hydroxybenzoic acid (compare Hübner, this vol., i, 366). G. T. M.

Condensation of Ethylic Malonate with Acetone. By ALEXANDER MEYENBERG (*Ber.*, 1895, **28**, 785—787).—Ethylic malonate (1 mol.) and acetone (1 mol.), when heated for 14 hours at 100° with acetic anhydride (1 mol.) and a little zinc chloride, condense to *ethylic isopropylenemalonate*, $CMe_2{:}CH(COOEt)_2$. This is a colourless liquid, boiling at 175—178° under 120 mm. pressure; when hydrolysed with 40 per cent. aqueous potash, it yields the *acid*, which melts at 170—171°. C. F. B.

Ethylic Dicarboxyglutaconate. By SIEGFRIED RUHEMANN and A. P. SEDGWICK (*Ber.*, 1895, **28**, 822—825).—Ethylic dicarboxyglutaconate reacts with methylamine in the same manner as with aniline (this vol., i, 20), the products being *ethylic methylamidoethylenedicarboxylate*, $NHMe{\cdot}CH{:}C(COOEt)_2$, melting at 34°, and the methylamide of malonic acid. Ethylenediamine behaves in a similar manner, *ethylic ethylenediamidodiethylenetetracarboxylate*,

$$C_2H_4[NH{\cdot}CH{:}C(COOEt)_2]_2,$$

which crystallises in prisms melting at 126°, being formed along with ethylenemalonamide. *Ethylic metaphenylenediamidodiethylenetetracarboxylate*, $C_6H_4[NH{\cdot}CH{:}C(COOEt)_2]_2$, is obtained when metaphenylenediamine is employed. It crystallises in needles, and melts at 110°. Formamide, on the other hand, converts ethylic dicarboxyglutaconate into *ethylic dihydroxypyridinedicarboxylate*,

$$\begin{array}{l} C(OH){\cdot}C(COOEt){:}CH \\ \| \qquad\qquad\quad | \\ N\text{——}C(OH)\text{═}C{\cdot}COOEt' \end{array}$$

which crystallises in slender, colourless needles, and melts at 201°. This substance combines with bromine to form a yellow additive compound, which loses all its bromine in a vacuum. A. H.

Dibasic Ketonic Acid, $C_{10}H_{14}O_6$. By E. HOFACKER and EDUARD A. KEHRER (*Ber.*, 1895, **28**, 917—921).—The preparation of δ-furfurylidenelevulinic acid has been previously described (Abstr., 1893, i, 254); it is separated from βδ-difurfurylidenelevulinic acid by repeated treatment with hot water, in which the latter is less soluble. By the action of hydrogen chloride on the δ-acid in alcoholic solution, *ethylic para-φ-diketosebate*, $C_2H_4(CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt)_2$, is formed; it

crystallises in colourless, lustrous, rhombic plates, and melts at 46°. The *methylic salt* resembles the preceding compound, and melts at 92°. The *acid* is most readily prepared by hydrolysis of the ethereal salts with concentrated hydrochloric acid; it crystallises from water in colourless plates, melts at 156—157°, reduces Fehling's solution when heated, becomes yellow with sulphuric acid, and yields iodoform. The *silver salt* is amorphous; the *zinc salt* forms silvery plates. By the action of alcoholic potash on the above ethereal salts, the preceding compound is formed, together with a second acid, which dissolves more readily in ether, and is obtained as a bye-product during the preparation of the ethereal salts. It melts at 89—90°, yields crystalline *calcium* and *zinc salts*, and is being further investigated. J. B. T.

Formation of Propyltartronic acid from Dibutyryl dicyanides. By KARL BRUNNER (*Monatsh.*, 1894, **15**, 747—774; compare Abstr., 1893, i, 553).—*Propyltartronic acid*, $CH_2Et\cdot C(OH)(COOH)_2$, prepared from the dibutyryl cyanide obtained from normal butyric anhydride, crystallises in monoclinic plates containing $1H_2O$, melts at 52—56°, and decomposes with evolution of gas at 105°. The anhydrous acid melts at 122°, is soluble in water and alcohol, and on distillation yields carbonic anhydride and α-hydroxyvaleric anhydride.

Isopropyltartronic acid, $CHMe_2\cdot C(OH)(COOH)_2$, obtained from isobutyric anhydride, melts and decomposes at 149°, and is converted at 150° into carbonic anhydride and α-hydroxyisovaleric acid, which melts at 83° (compare this vol., i, 21). G. T. M.

Action of Ammonia on Ethylic Oxalacetate. By WILHELM WISLICENUS and WALTER BECKH (*Ber.*, 1895, **28**, 788—791).—Ammonia combines with ethylic oxalacetate in cold alcoholic or ethereal solution forming a compound $COOEt\cdot C(ONH_4):CH\cdot COOEt$ or $COOEt\cdot C(OH)(NH_2)\cdot CH_2\cdot COOEt$. This is a white, crystalline powder, which melts at 83°, and exhibits many of the reactions of an ammonium salt; it readily decomposes when kept or when heated, yielding the ammoniumtriethylic salt of aconitoxalic acid,

$$COOEt\cdot CH:C(COONH_4)\cdot CH(COOEt)\cdot CO\cdot COOEt$$

(Claisen and Hori, Abstr., 1891, 424). This *ammonium salt* melts at 129°, the barium salt at 213—215°; the *calcium salt* crystallises with $2H_2O$. C. F. B.

Butanetetracarboxylic Acids. By KARL AUWERS and TITUS V. BREDT (*Ber.*, 1895, **28**, 882—890; compare Abstr., 1894, i, 362).—Butanetetracarboxylic acids are formed only in small quantity by the action of iodine on ethylic sodioethenyltricarboxylate; the hexacarboxylate, which is first obtained, is hydrolysed and carbonic anhydride eliminated. The acids were therefore prepared in the manner previously described (*h* and *n* signifying the acid of higher and of lower melting point).

The *n-tetramide*, $C_4H_6(CONH_2)_4$, is readily obtained by the interaction of the *n*-tetramethylic salt and ammonia, or by heating the

acid with alcoholic ammonia at 135—145°; at higher temperatures resinous products are formed, at lower temperatures unaltered ammonium salt separates. The compound is very sparingly soluble, crystallises in rhombic plates, turns brown at 280°, and chars without melting at about 310°; it is hydrolysed by prolonged boiling with potash.

The *n-diamic acid*, $C_4H_6(COOH)_2(CONH_2)_2$, prepared by the action of ammonia on the diethylic salt, is purified by means of its crystalline *sodium salt*, and is deposited in thin plates melting and evolving gas at 181°; it is rapidly decomposed by water, and is insoluble in other media. The *diimide*, $C_4H_6\left(\begin{matrix}CO\\CO\end{matrix}>NH\right)_2$, is prepared by heating the preceding compound above its melting point, and is formed together with the tetramide, from which it is separated by its solubility in nitrobenzene; it is sparingly soluble, crystallises from water in small, hexagonal plates, and chars at about 320° without melting. The imide is soluble in soda and ammonia; its *silver salt* is white and sparingly soluble; when reduced, it is converted into an oily base which has a characteristic odour and yields a crystalline *platinochloride*.

The *dianilic acid*, $C_4H_6(COOH)_2{\cdot}(CO{\cdot}NHPh)_2$, is prepared from the anhydride (m. p. 247°) and aniline; it crystallises in broad, truncated needles, melts, when rapidly heated, at 187°, and evolves gas at 190°. The *diphenylimide*, $C_4H_6\left(\begin{matrix}CO\\CO\end{matrix}>NPh\right)_2$, is formed by heating the preceding compound at about 190°, and is deposited from dilute acetic acid in rhombic crystals melting at 194—197°. The *tetraphenylhydrazide*, $C_4H_6(CO{\cdot}NH{\cdot}NHPh)_4$, prepared from the tetrethylic salt and phenylhydrazine, is sparingly soluble, forms small, colourless prisms, and melts above 280°.

All attempts to prepare the *h*-tetramide were unsuccessful. *Diethylic h-butanetetracarboxylate*, $C_4H_6(COOH)_2{\cdot}(COOEt)_2$, is formed by the action of hydrogen chloride on the *h*-acid in alcoholic solution at 0°; it is a colourless oil, and when treated with ammonia yields the *h-diamide*, which closely resembles the isomeric compound, is even more readily hydrolysed, and melts at 169°. When heated above its melting point, or by the action of alcoholic ammonia on the *h*-acid at 135—145°, the diimide is formed (see above), proving the previous conversion of the *h*- into the *n*-acid. The *h-dianilic acid*, prepared from aniline and the anhydride (m. p. 168°), crystallises in long, slender needles, and melts at 167°. When heated above its melting point, a compound is formed, which appears to be a mixture of *h*- and *n*-diphenylimides, it crystallises in plates, softens at 180°, and melts between 210° and 230°. The *h-tetraphenylhydrazide* crystallises in small, slender, colourless needles, and melts above 280°.

Both the butanetetracarboxylic acids combine with resorcinol or dimethylmetamidophenol; the resulting dyes resemble those from succinic acid. J. B. T.

Dimethylvioluric acid and Dimethylnitrobarbituric acid. By Rudolf Andreasch (*Monatsh.*, 1895, **16**, 17—33; compare Abstr.,

1879, 618, and Techow, this vol., i, 83).—Dimethylvioluric acid (dimethylisonitrosomalonylcarbamide), $CO<^{NMe\cdot CO}_{NMe\cdot CO}>C:N\cdot OH$, prepared from dimethylalloxan and hydroxylamine hydrochloride at 100°, crystallises from water in needles which contain $1H_2O$ and melt at 141°. It forms a neutral *potassium* salt, which crystallises in shining, violet scales; an *acid potassium* salt, $C_6H_6KN_3O_4,C_6H_7N_3O_4$, which forms slender, orange-red needles; a *sodium* salt, with $4H_2O$, which crystallises in peach-blossom-red needles; an *acid sodium* salt, $C_6H_6NaN_3O_4,C_6H_7N_3O_4$, which crystallises in orange-red needles; an *ammonium* salt, in red needles; a *barium* salt, with $4H_2O$, which crystallises in garnet-red scales; and a *strontium* salt, with $2H_2O$, which crystallises in red needles. The *zinc*, *lead*, *cadmium*, and *silver salts* are all coloured and crystallise well, and the *ferrous salt* yields a dark blue aqueous solution.

Dimethylnitrobarbituric acid, $CO<^{NMe\cdot CO}_{NMe\cdot CO}>CH\cdot NO_2$, is obtained on mixing together dimethylvioluric acid and nitric acid. It dissolves in 5·98 parts of water at 14°, and separates from the solution in needles or in crystalline masses, melts with decomposition at 131—132°, and yields the following salts:—A *potassium* salt, $C_6H_6N_3O_5K$, which crystallises in greenish-yellow needles; a *sodium* salt, with $1H_2O$, in yellow needles; an *ammonium* salt, crystallising in slender needles; a *calcium* salt, in flat prisms; a *barium* salt, with $2H_2O$, in rosy-red, flat needles; a *strontium* salt, crystallising in light cornflower-blue masses; a *magnesium* salt, with $4H_2O$, which crystallises in yellowish-green needles; a *lead* salt, in bright yellow scales; and a *silver* salt, which forms violet-grey prisms. G. T. M.

Synthesis of Sulphones from Sodium Alkylic Sulphinates by the Action of Potassium Alkylic Sulphates. By Robert Otto (*Annalen*, 1895, **284**, 300—306).—In the well-known synthesis of sulphones by acting on sodium alkylic sulphinates with alkylic haloïds, it is found that the latter may be replaced by potassium alkylic sulphates. The method, however, is only of theoretical interest, and has no practical advantages over the older process. M. O. F.

Thiophen Derivatives. By Eugen Baumann and Emil Fromm (*Ber.*, 1895, **28**, 890—895).—Paradimethoxystilbene is readily converted into paratetramethoxytetraphenylthiophen by heating with sulphur; other compounds with the group CH:CH readily react, but saturated compounds are unaltered, or practically so, even at very high temperatures.

Cinnamic acid and sulphur, when heated at 240°, evolve hydrogen sulphide and carbonic anhydride; the product, after purification, melts at 126—128°, and consists of 2 : 5- and 2 : 4-*diphenylthiophens*, which can be separated by crystallisation from alcohol and acetone; the former melts at 152° and is already known; the latter melts at 119—120°, crystallises in colourless, lustrous plates, and differs but little

in solubility from the isomeric compound; its constitution is shown by its formation from anhydrotriacetophenone bisulphide,

$$CPhMe<\begin{matrix}S\text{——}CPhMe\\ S\cdot CPh{:}CH\end{matrix}$$

(compare this vol., i, 362). Sulphur dissolves in boiling cinnamene, and at 190—195° evolution of hydrogen sulphide commences, above 200° ethylbenzene is formed, and the residue consists of 2 : 4-diphenylthiophen together with the 2 : 5-isomeride in very small quantity.

J. B. T.

Formation of Carbon Rings: Conversion of Pimelic into Cyclopentenedicarboxylic acid. By RICHARD WILLSTÄTTER (*Ber.*, 1895, **28**, 655—665; compare Haworth and Perkin, Trans., 1894, 978).—$\alpha_1\alpha_2$-*Dibromopimelic acid*, $COOH\cdot CHBr\cdot[CH_2]_3\cdot CHBr\cdot COOH$, is obtained by heating pimelic acid with bromine and phosphorus; it melts at 140—142°, and is very soluble in alcohol and ether, dissolving with difficulty in cold water but more readily in hot. It resists the action of hot aqueous soda, and does not yield silver bromide when boiled with fuming nitric acid in presence of silver nitrate. The *diethylic* salt is a heavy, colourless oil which boils at 224° (corr.) under a pressure of 28 mm.

Δ^1-1 : 2-Cyclopentenedicarboxylic acid, obtained by the action of sodium ethoxide on diethylic dibromopimelate, is identical with dihydropentenedicarboxylic acid (*loc. cit.*). The *anhydride* is a colourless oil which yields the acid on treatment with boiling water. The normal *silver* salt, $C_7H_6O_4Ag_2$, is obtained as a white precipitate on adding silver nitrate to a neutral solution of the sodium salt. $\alpha_1\alpha_2$-Dibromo-1 : 2-cyclopentanedicarboxylic acid (*loc. cit.*) is obtained by allowing the unsaturated acid to remain in an atmosphere of bromine vapour. When heated with concentrated aqueous potash, cyclopentenedicarboxylic acid is converted into adipic acid.

The *ethylic* salt of dibromosuberic acid is a colourless oil which boils at 233—236° (corr.) under a pressure of 26 mm. When treated with sodium ethoxide, it yields diethoxysuberic acid together with a small quantity of dihydroxysuberic acid; tetrahydrophthalic acid is not present in the mixture.

M. O. F.

Hexamethylene Derivatives. By ALPHONSE COMBES (*Bull. Soc. Chim.*, 1894, [3], **11**, 710—717).—*Triethyltriketohexamethylene* (*triethylphloroglucinol*), $CO<\begin{matrix}CHEt\cdot CO\\ CHEt\cdot CO\end{matrix}>CHEt$, is obtained by heating pure butyric and aluminium chlorides together at 60°, and is insoluble in water, but soluble in chloroform; it melts at 107°, and boils at 216° (15 mm.). If the reaction is carried out in chloroform solution, the yield is very small, the main products being butyric acid and butyrone, possibly from the decomposition of an intermediate product, α-butyrylbutyric chloride.

Triethylphloroglucinol behaves as a monobasic acid, the mon-alkali salts being neutral; other more basic salts probably exist, as heat is developed on the addition of more alkali. It does not react with the

usual reagents for hydroxyl, and is stable towards potash at 100°, but it is completely hydrolysed by 25 per cent. aqueous potash at 150—160° into butyrone, butyric acid, and carbonic anhydride; phloroglucinol behaves in a precisely similar manner under the same conditions, yielding acetone and acetic acid. The *phenylhydrazone* crystallises with difficulty. When triethylphloroglucinol is distilled with zinc dust, it is reduced to various hydrocarbons, including a small quantity of triethylbenzene, in this also resembling phloroglucinol, which yields only a small quantity of benzene under the same conditions. The behaviour towards ferric chloride, too, is similar to that of phloroglucinol, there being no coloration except in concentrated solutions.

The formation of the ring may possibly result from condensation of an intermediate product, $COPr^{\alpha}\cdot CHEt\cdot CO\cdot CHEt\cdot COCl$.

JN. W.

Diketohexamethylene from Succinic acid. By FRANZ FEIST (*Ber.*, 1895, **28**, 738—741).—Anhydrous calcium succinate was heated in a Meer's retort, and the distillate distilled with steam; the residue was repeatedly treated with hot water, and the ketone isolated from the solution by means of sodium hydrogen sulphite. The compound was identified by its action on Fehling's solution and potassium permanganate, by the preparation of the characteristic phenylhydrazone, and by the formation of quinone when treated with ferric chloride. The yield was only 0·4—0·5 gram from 1 kilo. of succinic acid.

J. B. T.

Synthesis of Naphthenes. By NICOLAI D. ZELINSKY (*Ber.*, 1895, **28**, 780—783).—By distilling dimethylpimelic acid (Abstr., 1892, 430) with lime, 1 : 3-*dimethylketohexamethylene*, $CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CO$, is obtained; it boils at 173—174°, yields an *oxime* melting at 104—105°, and can be reduced to a *secondary alcohol* boiling at 174·5° under 755 mm. pressure. This yields an *iodide*, by reduction of which 1 : 3-*dimethylhexamethylene*, $CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CH_2$, can be obtained.

1 : 3-Dimethylhexamethylene boils at 119·5° under 751 mm. pressure, and has a sp. gr. = 0·7688 at 19°/0°; it is probably identical with Markovnikoff's α-octonaphthene from Caucasian naphtha. Its reactions are those of a saturated aliphatic hydrocarbon; with bromine and aluminium bromide, however, it yields tetrabromo-1 : 3-xylene, and with a mixture of nitric and sulphuric acids, it yields a trinitro-1 : 3-xylene.

C. F. B.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **51**, 444—446; compare Abstr., 1894, i, 325, 501).—Among the diamido- and dihydroxy-benzenes the meta-derivative is the most soluble, the para-derivative being the least soluble; so, also, terephthalic acid is the least soluble of the three dicarboxylic acids, but the ortho-acid is more soluble than the meta-acid. A comparison

may be drawn between the solubility of the phthalic acids and that of the dicarboxylic acids of the fatty series. For, according to the author's configuration for benzene (Abstr., 1894, i, 326), fumaric acid has a similar structure to terephthalic acid, maleïc acid to the meta-acid, and acetylenedicarboxylic acid to the ortho-acid; it may thus be expected that the order of solubility will be acetylenedicarboxylic acid, maleïc acid, fumaric acid; and this is found to be the case.

The author can also explain the exceptional behaviour of ortho-toluidineparasulphonic acid towards acetic anhydride (Abstr., 1884, 1024), and the difference in the solubilities of the aniline and toluidine sulphonic acids, by reference to his formula for benzene.

A. G. B.

Alteration of Phenol by the Action of Light and the Formation of Hydrogen Peroxide. By A. Bach (*Chem. Centr.*, 1894, ii, 318; from *Mon. Sci.*, [4], **8**, 508—510).—It is well known that pure phenol by the action of light and air is gradually coloured red to brown, and this alteration has been attributed to the formation of hydrogen peroxide, which can usually be detected in the altered phenol. The author has found that when phenol is exposed to the action of light and moisture in an atmosphere of carbonic anhydride, it is quickly turned red, and no trace of hydrogen peroxide can be detected. On the other hand, when phenol is exposed to light and damp air, and care is taken to exclude carbonic anhydride, after three days only a faint, brownish coloration is observed, and hydrogen peroxide can then be detected by its characteristic reactions. Whence the author concludes that the alteration of the phenol is not due to the formation of hydrogen peroxide. E. C. R.

Aromatic Arsenites. By P. Fromm (*Ber.*, 1895, **28**, 620—623).—*Triphenylic arsenite* is prepared by adding arsenic trichloride dissolved in ether to sodium phenoxide suspended in the same medium. It is a colourless, viscous liquid of sp. gr. 1·354 at 20°; it boils at 275° under a pressure of 57 mm., and has the odour of phenol. The salt is decomposed by water into phenol and arsenious anhydride, whilst the action of chlorine and bromine gives rise to substituted derivatives of phenol.

Triparatolylic arsenite is prepared by a similar method, xylene being employed instead of ether. It is a colourless, oily liquid of sp. gr. 1·2794 at 13°; it boils at 290° under a pressure of 20 mm., and is readily decomposed by water.

Tri-β-naphthylic arsenite crystallises in long, colourless needles, and melts at 113—114°; boiling water decomposes it into β-naphthol and arsenious anhydride.

Tribenzylic arsenite is a yellow, viscous liquid which partly decomposes when distilled at 200° under a pressure of 20 mm. Benzylic alcohol and arsenious anhydride are formed when the salt is treated with water, and the action of bromine gives rise to bromobenzoic acid, benzylic bromide, arsenious anhydride, and arsenic tribromide. M. O. F.

Some Selenium Derivatives of Anisoïl and Phenetoïl. By FRANZ KUNCKELL (*Ber.*, 1895, **28**, 609—612).—When selenyl chloride, SeO_2Cl_2 (1 mol.), is added slowly to an ethereal solution of anisoïl (2 mols.), *dichloroselenoanisoïl*, $SeCl_2(C_6H_4{\cdot}OMe)_2$, and *selenoanisoïl*, $Se(C_6H_4{\cdot}OMe)_2$, are obtained. The former crystallises in yellow needles, and melts at 159°; the latter in white nacreous plates, melting at 48°. The latter, in chloroform solution, unites with chlorine to form the first-mentioned compound; with bromine to form *dibromoselenoanisoïl*, brick-red needles, melting at 124°, whilst with iodine it yields a red syrup. By treating the halogen compounds with moist silver oxide, they can be converted into *dihydroxyselenoanisoïl*,

$$Se(OH)_2(C_6H_4{\cdot}OMe)_2,$$

which crystallises in white needles, and melts at 137°.

An analogous series of compounds can be prepared from phenetoïl, $C_6H_5{\cdot}OEt$. *Selenophenetoïl*, white needles, m. p. 56°. *Dichloroselenophenetoïl*, yellow needles, m. p. 140°. *Dibromoselenophenetoïl*, red needles, m. p. 123°. *Diiodoselenophenetoïl*, coffee-coloured needles, m. p. 96°. *Dihydroxyselenophenetoïl*, white needles, m. p. 145°.

C. F. B.

Anethoïl. By CARL HELL (*J. pr. Chem.*, 1895, [2], **51**, 422—424).—Some prefatory remarks to the following paper (see next abstract). The question whether anethoïl contains propenyl, $\cdot CH{:}CHMe$, or allyl, $\cdot CH_2{\cdot}CH{:}CH_2$, receives additional importance from Eijkman's researches on the conversion of allylbenzene into propenylbenzene derivatives (Abstr., 1890, 748), and from Grimaux's observation that essence of tarragon does not contain anethoïl, but an isomeride, estragoïl, and that anethoïl is probably a stereoisomeride of Eijkman's methylchavicol (Abstr., 1894, i, 120).

A. G. B.

Action of Bromine on Anethoïl. By CARL HELL and G. GÄRTTNER (*J. pr. Chem.*, 1895, [2], 424—434; compare preceding abstract).—*Bromanethoïl dibromide*, $OMe{\cdot}C_6H_3Br{\cdot}C_3H_5Br_2$, is obtained by dropping bromine into a well-cooled ethereal solution of anethoïl, evaporating, washing with alcohol, and crystallising from light petroleum. It forms thick, strongly refractive needles, melts at 107—108°, and dissolves easily in benzene, chloroform, and carbon bisulphide. Zinc dust removes 2 atoms of bromine from the compound, producing a white powder which is probably a polymeride of bromanethoïl, for the same substance is formed when anethoïl is polymerised with strong sulphuric acid and treated with bromine in ethereal solution. The oxidation of bromanethoïl dibromide by chromic acid in glacial acetic acid leads to the formation of a *dibromoketone*, to which the formula $OMe{\cdot}C_6H_3Br{\cdot}CO{\cdot}CHBrMe$ or $OMe{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}COMe$, must be assigned if bromanethoïl dibromide be a propenyl derivative of the form

$$OMe{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CHBrMe,$$

but which must have the constitution $OMe{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CO{\cdot}CH_2Br$, if bromanethoïl dibromide be an allyl derivative of the form

$$OMe{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br.$$

Its constitution remains unsettled, but the weight of evidence is in favour of the second of those given; the compound crystallises from light petroleum in yellowish laminæ, and from alcohol in slender, white needles; melts at 98°, and is very soluble in glacial acetic acid, benzene, chloroform, and carbon bisulphide. By treatment with zinc dust in alcohol, the dibromoketone loses the bromine from the side-chain, and yields the corresponding *bromoketone*,

$$OMe\cdot C_6H_3Br\cdot CH_2\cdot COMe,$$

which crystallises in colourless needles, melts at 99°, and is freely soluble in ether, benzene, glacial acetic acid, and chloroform.

When the dibromoketone is heated with potassium acetate in alcoholic solution, it yields an *acetyl* derivative, $OMe\cdot C_6H_3Br\cdot C_3H_4O_2Ac$. When similarly treated with ammonia, it yields orange-yellow crystals and yellowish-white crystals; the latter can be separated from the former by their insolubility in cold glacial acetic acid, and, when recrystallised from the hot acid, melt at 210—211°.

When the dibromoketone is oxidised with potassium permanganate, bromanisic acid [COOH : Br : OMe = 1 : 3 : 4] is obtained, a result which settles the orientation of the nucleal bromine atom. A ketonic acid was also obtained by the oxidation of the ketone derived from the anethoïl with which the authors worked, but the ketone from a sample of anethoïl which had been specially prepared from star-anise oil did not yield such an acid. A. G. B.

Action of Sulphuryl Chloride on Phenols and their Ethers. By Alberto Peratoner and A. Genco (*Gazzetta*, 1894, **24**, ii, 375—396).—Peratoner and Finocchiaro (Abstr., 1894, i, 368) have shown that in the chlorination of phenol, resorcinol, and phloroglucinol by sulphuryl chloride, the chlorine enters the molecule in the para-position relatively to the hydroxyl groups. Quinol should therefore not react with sulphuryl chloride; this is found to be the case if no solvent is employed, but on treating with sulphuryl chloride in ethereal solution, *orthodichloroquinol*, $C_6H_2Cl_2(OH)_2$, is formed. It crystallises from water in long, reddish needles containing $2H_2O$, which are lost at 100°; it melts at 144°, and sublimes unchanged. Its *dibenzoyl* derivative, $C_6H_2Cl_2(OBr)_2$, crystallises in colourless scales melting at 173—174°.

Orthodichloroquinone, $C_6H_2Cl_2O_2$, may be prepared by oxidising the corresponding hydroxyl derivative by Clark's method; it crystallises in yellow laminæ or needles melting at 96°, and is volatile in a current of steam.

On chlorinating quinol with smaller quantities of sulphuryl chloride than that used above, quinhydrone, monochloroquinol, quinone, its di- and tetra-chlorides, and chloranil are formed.

Monochloroquinol dichloride, $C_6H_3Cl_3O_2$, is obtained by the action of sulphuryl chloride on an ethereal solution of the monochloroquinol melting at 104—105°; it forms colourless laminæ which do not melt but sublime at 195—200°. When heated with acetic acid or dilute alcohol, it yields a mixture of the meta- and para-dichloroquinols; it

therefore has the constitution $\begin{matrix}CH\cdot CO\cdot CHCl\\ \|\\ CCl\cdot CO\cdot CHCl\end{matrix}$; no tetrachloride could be prepared, chloranil resulting from the further action of sulphuryl chloride.

Quinone dichloride is converted into a mixture of orthodichloroquinol and monochloroquinol by sulphurous acid. Monochloroquinol and quinone tetrachloride under similar conditions yield trichloroquinol. W. J. P.

Formation of Tetrachloroquinone from Hexachlorophenol. By Etienne Barral (*Bull. Soc. Chim.*, 1894, [3], **11**, 705—710).—α-Hexachlorophenol is hydrolysed by water or acids into tetrachloroquinone and pentachlorophenol, but is converted by chromic acid into the latter substance alone. When heated with water for 24 hours at 160—165°, carbonic anhydride is liberated, and after the pentachlorophenol and unchanged hexachlorophenol have been dissolved out with light petroleum, the residual tetrachloroquinone merely requires to be washed with water. The yield is not large, but the product is very pure. A quantitative yield is obtained by heating the well-powdered substance with five or six times its weight of concentrated sulphuric acid, diluted with 1 or 2 per cent. of water. The product is washed with water, and dried at the ordinary temperature, no organic bye-products being formed. Jn. W.

Action of Alkalis on Brominated Derivatives of Phloroglucinol. By Josef Herzig and J. Pollak (*Monatsh.*, 1894, **15**, 700—704).—In contrast to the behaviour of tribromophloroglucinol, the true bromo-compounds of phloroglucinol derivatives, such as tribromodiethylphloroglucinol (m. p. 62—64°) and tribromotriethylphloroglucinol (m. p. 102—104°), are perfectly stable in presence of boiling solutions of caustic alkalis. Tribromotriethylphloroglucinol, when heated in sealed tubes with alcoholic potash at 140°, loses no bromine, but is converted into tribromodiethylphloroglucinol. A considerable quantity of phloroglucide, $C_{12}H_{10}O_5 + 2H_2O$, is formed as a bye-product in the preparation of diethylphloroglucinol (compare Will and Albrecht, *Ber.*, **17**, 2098). G. T. M.

Paramidobenzylic Alcohol. By Otto Fischer and Gustav Fischer (*Ber.*, 1895, **28**, 879—881; compare Abstr., 1891, 695).—The substance obtained after reducing paranitrobenzylic acetate with stannous chloride, and removal of the tin by hydrogen sulphide, is shown to be diparamidobenzylic sulphide, $C_{14}H_{16}N_2S$, and not paramidobenzylic alcohol. The pure substance melts at 104—105°, and not at 95° as previously stated. Its formation is due to the action of the hydrogen sulphide on the amido-alcohol which is first formed. It forms a hydrochloride, $C_{14}H_{16}N_2S,2HCl$, and a hydrobromide,

$$C_{14}H_{16}N_2S,2HBr.$$

Paramidobenzylic alcohol may be obtained by reducing a neutral solution of the nitro-alcohol with zinc dust. It forms large, colourless plates, melts at 65°, and readily reacts with aldehydes forming

condensation products. The *benzylidene* compound crystallises in yellowish plates melting at 67—68°.

o-*Hydroxybenzylideneamidobenzylic alcohol*, from salicylaldehyde and the amido-alcohol, forms golden plates and melts at 155°.

Benzoylamidobenzylic alcohol forms colourless crystals and melts at 150—151°.

The amido-alcohol may readily be converted into diparamidobenzylic sulphide by saturating an acidified solution of the alcohol with hydrogen sulphide. J. J. S.

Reduction of Nitrobenzylic Chloride. By Otto Dimroth and Johannes Thiele (*Ber.*, 1895, **28**, 914—916).—When ortho- and para-nitrobenzylic chlorides are reduced with stannous chloride at low temperatures, and the product treated with hydrogen sulphide, they yield the corresponding diamidobenzylic sulphides; the ortho-compound has been described by Jahoda and also by Gabriel (this vol., i, 190); the para-derivative is identical with the "paramidobenzylic alcohol" prepared by O. and G. Fischer (Abstr., 1891, 695, and preceding abstract). Both compounds readily lose hydrogen sulphide when treated with salts of the heavy metals. The nature of the action by which the sulphides are formed is not understood; probably the intermediate compounds $C_6H_4<\begin{matrix}CH_2\\|\\NH\end{matrix}$ [$CH_2:NH = 1:4$ and $1:2$] are first produced; it is improbable that the chlorides, acetates, or alcohols directly condense with hydrogen sulphide, and direct experiments with orthamidobenzylic alcohol and orthamidobenzylic chloride confirm this. J. B. T.

Cyaphenine; Substituted Benzonitriles. By Adolph Claus (*J. pr. Chem.*, 1895, [2], **51**, 399—414).—Trinitrocyaphenine crystallises in small needles, and is nearly insoluble in all ordinary solvents. It melts and decomposes between 250° and 260°; unlike cyaphenine, it is very easily hydrolysed, metanitrobenzoic acid being produced.

Attempts to polymerise the nitrobenzonitriles by treating them with fuming sulphuric acid failed, a more deeply-seated reaction occurring in each case, and a study of the polymerisation of benzonitrile itself by this method showed that the highest yield was 10 per cent. of cyaphenine.

Metanitrobenzonitrile yields metanitrobenzamide when warmed with sulphuric acid; the amide melts at 143° and boils at 310—315°; its crystallographical measurements are given. When the nitrile is treated with fuming sulphuric acid, it yields *dimetanitrobenzoylimide*, $(NO_2\cdot C_6H_4\cdot CO)_2NH$, which crystallises in colourless tablets, and usually melts at 199°, but at 120° when it is kept at this temperature for a long time, and at 80° when allowed to solidify again; it is very sparingly soluble except in glacial acetic acid and in acetone; its crystallographical measurements are given.

With ordinary sulphuric acid, paranitrobenzonitrile behaves similarly to the meta-derivative, but with the fuming acid it suffers a more deeply-seated change, the nature of which was not determined.

Orthonitrobenzonitrile is more easily attacked by sulphuric acid than are its isomerides, and the change which occurs is of a complex character. By using an acid of sp. gr. 1·6 the nitrile can be converted into orthonitrobenzamide, which melts at 174° and distils unchanged at 317°.

Sodium is practically without action on metanitrobenzonitrile in ether; similarly, this nitrile is remarkably stable towards nitrating agents and bromine. Attempts to polymerise the halogen-benzonitriles have also failed.

It is already known that the presence of a nitro-group in the ortho- or para-position relatively to the amido-group of a substituted aniline renders diazotisation of the compound difficult, and that pentabromaniline is not susceptible of diazotisation; since, on the other hand, the symmetrical trihalogen-anilines do not show this difficulty, it is surprising to find that 2 : 3 : 5 : 6-*tetrabromaniline* behaves like pentabromaniline towards diazotising agents. This tetrabromaniline was prepared by reducing *tetrabromonitrobenzene*, [$NO_2 : Br_4 = 1:2:3:5:6$], which crystallises in small, colourless laminæ, and melts at 168°; the aniline forms colourless needles, melts at 130°, and yields bromanil by oxidation.

The author concludes with some remarks on the mechanism of the hydrolysis of nitriles into acids, a reaction which, he believes, occurs in two stages—the formation of an amide and the hydrolysis of this (compare Sudborough, Proc., 1895, 74). A. G. B.

Hydrolysis of Aromatic Nitriles. By John C. Cain (*Ber.*, 1895, **28**, 967—969).—Dinitrodurene, $C_6Me_4(NO_2)_2$ [$NO_2 : NO_2 = 1:4$], is obtained by nitrating durene at 15° in presence of a large excess of fuming sulphuric acid. In addition to diamidodurene, which melts at 149°, reduction with zinc dust and glacial acetic acid gives rise to *amidonitrodurene*, which crystallises from alcohol in yellow needles and melts at 158—159°. This is converted by means of the Sandmeyer reaction into the *nitrile* of nitrodurenecarboxylic acid, which crystallises from alcohol in white needles and melts at 160°. Attempts to hydrolyse the nitrile with hydrochloric acid have not hitherto been successful, although an acid *substance* melting at 105° has been obtained by the action of soda. M. O. F.

Reduction of Amidonitriles. By Attilio Purgotti (*Gazzetta*, 1894, **24**, ii, 427—431).—On reducing the amidonitrile prepared from the cyanhydrin of benzaldehyde with zinc dust and hydrochloric acid, a base is obtained; the analyses of the platinochloride and of the benzoyl derivative point to its being *phenylethylenediamine*,

$$NH_2 \cdot CHPh \cdot CH_2 \cdot NH_2.$$

The investigation is being continued. W. J. P.

Action of Thionylaniline on the Xylylenediamines. By Fez. Düring (*Ber.*, 1895, **28**, 600—608).—The xylylenediamines, $C_6H_4(CH_2 \cdot NH_2)_2$, react with thionylaniline, SO:NPh, yielding

ammonia and aniline and a precipitate which consists of the thiosulphate and trithionate of the diamine, which are soluble in water, and amidotolualdehyde, $CHO\cdot C_6H_4\cdot CH_2\cdot NH_2$, which is insoluble. In the 1 : 2-series this precipitate is entirely soluble in water, and contains no amidotolualdehyde, but dihydroisoindole, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>NH$, instead, and diamine sulphate in place of thiosulphate. With sulphurous anhydride, the diamines, in ethereal solution, yield dithionamic acids, $C_6H_4(CH_2\cdot NH\cdot SO_2H)_2$; but these, especially the 1 : 2-derivative, readily lose SO_2, forming the monothionamic acids,

$$NH_2\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot SO_2H,$$

which yield crystalline compounds with benzaldehyde (1 mol.).

The *phenylhydrazones* of 1 : 3- and 1 : 4-*amidotolualdehyde* are yellow, and melt respectively at 253° and 278°. The other substances are white and, so far as their behaviour when heated is described, either do not melt or are decomposed. C. F. B.

Action of Orthohydroxybenzylic Alcohol (Saligenin) on Aromatic Diamines. By Carl Paal and H. Reckleben (*Ber.*, 1895, **28**, 934—936; compare C. Paal and H. Senninger, Abstr., 1894, i, 450).—Primary diamines behave as monamines towards this alcohol, condensing with it to products of the type

$$OH\cdot C_6H_4\cdot CH_2\cdot NHR.$$

These are rather unstable, crystalline substances, which decompose soon after melting, and are both phenolic and basic in character. The solutions in mineral acids give a blue thionine reaction with hydrogen sulphide and ferric chloride.

Orthohydroxybenzylorthophenylenediamine,

$$OH\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NH_2,$$

crystallises from alcohol in yellowish, concentrically grouped needles, and melts at 157°. It is sparingly soluble in water or light petroleum, easily in the other usual solvents, and in acids and alkalis; the acid solutions give a red coloration with ferric chloride. The *diacetyl* compound, $OAc\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NHAc$, from the base and the boiling acid or cold anhydride, crystallises from alcohol in white needles, and melts at 162°; it is slowly hydrolysed by acids and alkalis. The *triacetyl* derivative, obtained by acting on the base with boiling acetic anhydride, forms colourless, well-defined crystals, and melts at 133°; it is insoluble in alkalis and dilute acids, but is slowly hydrolysed by boiling alkalis. *Orthohydroxybenzylorthotolylenediamine*, $OH\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_3Me\cdot NH_2$ [$NH : NH_2 : Me = 1 : 2 : 4$ or $1 : 2 : 5$], crystallises in small, felted needles, and melts at 167°. *Orthohydroxybenzylparaphenylenediamine* is very unstable in presence of water. It crystallises from alcohol in small, yellow, concentrically grouped needles, and melts at 119°. Jn. W.

Benzenylamidothiophenol. By ERNEST NAEGELI (*Bull. Soc. Chim.*, 1894, [3], **11**, 893—897).—Benzenylamidothiophenol,

$$CPh\lessgtr^{N}_{S}>C_6H_4,$$

from benzanilide and sulphur, melts at 113° (uncorr.); (compare Hofmann, *Ber.*, **12**, 2360, and **13**, 1236). The *mononitro-derivative* melts at 188°, and on fusion with potash yields paranitrobenzoic acid; the nitro-group is therefore in the para-position relatively to the benzylic carbon. JN. W.

Mixed Amidines and Tautomerism. By HANS V. PECHMANN (*Ber.*, 1895, **28**, 869—879; compare Abstr., 1894, i, 452 and 457).—In previous papers, the author has shown that mixed phenyltolylformazyls, $C_7H_7\cdot N{:}N\cdot CR{:}N\cdot NHPh$ and $Ph\cdot N{:}N\cdot CR{:}NH\cdot C_7H_7$, are identical, so far as regards their physical and chemical properties. In the present paper, it is shown that mixed amidines and diazoamido-compounds also exist in only one form, even when prepared by different methods, but that they can give isomeric ethyl and benzoyl derivatives.

Phenylparatolylbenzenylamidine, $PhN{:}CPh\cdot NH\cdot C_7H_7$ or

$$C_7H_7\cdot N{:}CPh\cdot NHPh,$$

whether prepared from benzanilide and toluidine or from benzotoluidide and aniline, has the same properties, melts at 132—133°, and forms a *benzoyl* derivative which melts at 142° and is sparingly soluble in ether and alcohol.

Ethylparatolylamidophenylbenzenylimidine, $PhN{:}CPh\cdot NEt\cdot C_7H_7$, was prepared by acting on benzaniline with phosphoric chloride, and then treating the product with ethylparatoluidine. The base forms large, flat, six-sided prisms, and melts at 102°. The iodide melts at 226°.

Ethylphenylamidoparatolylbenzenylimidine, $C_7H_7\cdot N{:}CPh\cdot NEtPh$, obtained from benzotoluidide, phosphoric chloride, and ethylaniline, melts at 117°, and forms an iodide which melts at 226°. A mixture of equal parts of the two ethyl bases melts at 86°.

When the phenylparatolylbenzenylamidine, prepared by the two methods already given, was treated with ethylic iodide, a base was obtained in both cases, which melted at 86°, and was shown to be a mixture of the two ethylimidines (m. p. 102° and 117°).

Phenylparatolylethenylamidine, prepared from thioacetanilide and paratoluidine hydrochloride and also from parathioacetotoluidide and aniline hydrochloride, crystallises in plates which melt at 82—83°. It yields a *picrate*, melting at 146—147°, and a *benzoyl derivative*, melting at 96—97°. The latter is probably a mixture of the two possible isomerides, as, when decomposed by boiling with hydrochloric acid, it yields both benzanilide and benzotoluidide.

Diazoamidobenzenetoluene, prepared from diazobenzene and toluidine and also from diazotoluene and aniline, yields only a single acetyl derivative, *diazobenzeneparaacetotoluidide*, $PhN{:}N\cdot NAc\cdot C_7H_7$. This base melts at 140°, and, when decomposed by acids, yields aceto-

toluidide, but no trace of acetanilide. The corresponding *benzoyl derivative*, $PhN{:}N{\cdot}NBz{\cdot}C_7H_7$, melts at 124—125°, and, when treated with acids, yields benzotoluidide, but not benzanilide.

The author argues that substances of the general type

$$NHY{\cdot}R^{III}{:}NX \text{ and } NY{:}R^{III}{\cdot}NHX,$$

where $R^{III} = N$ (diazoamido compounds), CH (amidines) or N:CH·N (formazyl compounds), really exist in one form only, and that therefore the above formulæ cannot represent the structure of the molecule. J. J. S.

Stereoisomeric Diazocyanides. By Arthur Hantzsch and Otto W. Schulze (*Ber.*, 1895, **28**, 666—676).—The cyano-derivatives of the diazo-series hitherto known are additive compounds of the general formula $R{\cdot}N_2{\cdot}CN,HCN$, which are prepared by adding a diazotised solution of the base to an excess of a well-cooled solution of potassium cyanide. Diazobenzene cyanide hydrocyanide, $PhN_2{\cdot}CN,HCN$, has already been described by Gabriel; it crystallises in pale yellow needles, and melts at 70°.

Parachlorodiazobenzene cyanide hydrocyanide, $C_6H_4Cl{\cdot}N_2{\cdot}CN,HCN$, forms light brown needles melting at 103°, whilst the corresponding *paranitrodiazobenzene cyanide hydrocyanide* crystallises in orange-coloured needles and melts at 126°. These compounds do not react with R-salt to form colouring matters.

When a slight excess of potassium cyanide solution is added to a well-cooled diazo-solution, true diazocyanides are formed. These exist in two modifications, the relations between which have led the author to consider them as being stereoisomeric, in the same way as the syn- and anti-diazosulphonates.

Syn-chlorodiazobenzene cyanide, $\begin{matrix} C_6H_4Cl{\cdot}N \\ \| \\ CN{\cdot}N \end{matrix}$, is obtained, when the reaction is carried out at a temperature below −5°, in slender, yellow needles melting at 29°. It can be purified by dissolving it in alcohol below 0° and precipitating with ice-cold water. At the ordinary temperature, its alcoholic solution deposits the stereoisomeride of higher melting point. *Anti-chlorodiazobenzene cyanide*, $\begin{matrix} C_6H_4Cl{\cdot}N \\ \| \\ N{\cdot}CN \end{matrix}$, forms yellow needles or brown prisms melting at 105—106°, and is obtained by the reaction between potassium cyanide and the diazo-salt when the solution is not well cooled. The anti-cyanide is also produced when the syn-compound is preserved in the dry state. Both the compounds are volatile with steam and insoluble in water. The behaviour of the two isomerides with finely divided copper, prepared by Gattermann's method, is characteristically different. When the syn-form is added to the powder mixed with water and a little alcohol, a very violent evolution of nitrogen, accompanied by small explosions, occurs, *parachlorobenzonitrile*, which melts at 92°, being produced. The anti-cyanide, on the other hand, undergoes no change, and, when the mixture is heated, simply volatilises with the steam. The syn-derivative also appears to form metallic double cyanides much more

readily than the anti-form. The syn-cyanide readily gives an azo-colouring matter with β-naphthol in alcoholic solution, even in the absence of alkali, the product being identical with that obtained from the corresponding chloride. It also reacts in the usual way with R-salt, whilst the anti-cyanide does not yield colouring matters by either of these reactions. The syn-cyanide is converted by the action of aqueous alkalis into an additive product, which will be described in a subsequent communication.

Syn-nitrodiazobenzene cyanide is obtained at temperatures below −5°, and forms a yellowish-brown, microcrystalline precipitate, melting at 28—29°. It is still less stable than the corresponding chlorinated derivative, and rapidly passes into the anti-modification.

Anti-nitrodiazobenzene cyanide forms red needles, melting at 86°, and is remarkably stable. These two substances closely resemble the chloro-derivatives described above. With copper powder, the syn-compound at once yields paranitrobenzonitrile, whilst the anti-form is not altered. The syn-modification readily forms colouring matters, whilst the anti-form reacts with β-naphthol and R-salt in a characteristically different manner. The syn-derivatives both explode when heated, whilst the anti-compounds do not.

The author rejects the formula N:NR·CN for one of the isomerides on account of the lack of probability that such a substance would so readily undergo molecular change, and because the substance in question differs so markedly from the substituted ammonium cyanides, which possess the same grouping, but are readily soluble in water and decomposed by carbonic anhydride, whilst the diazo-cyanides are insoluble in water and are not decomposed by carbonic anhydride.

A. H.

Constitution of the Normal Diazo-compounds and of the Diazohalogen Salts. By ARTHUR HANTZSCH (*Ber.*, 1895, **28**, 676—687).—The author discusses the recently proposed formula $R\cdot N\begin{matrix}\diagup\!\!\diagup N\\ \diagdown Cl\end{matrix}$ for the unstable series of compounds which are isomeric with the true diazo-compounds. The nature of the tetrazolium compounds and of the substituted ammonium compounds, both of which contain a pentad nitrogen atom, is urged against this interpretation of the relations between the two isomeric series. The complicated nature of the change from the unstable to the stable form, which actually goes on with extreme readiness and without the intervention of other substances, points in the same direction, as does also the formation of ring compounds of the type $C_6H_4<\begin{matrix}N\\ O\end{matrix}>N$ from normal diazo-hydroxides without the sacrifice of their typical reactions.

The author considers that the halogen salts of the diazo-compounds must have a different constitution in the solid state from that which they have in aqueous solution.

The solid salts undergo gradual decomposition into nitrogen and the corresponding substituted hydrocarbon, when preserved at temperatures at which the solutions are quite unaltered. This is especially noticeable in the case of halogen-substituted diazo-salts.

Diiododiazobenzene chloride forms a lemon-yellow mass, which yields a neutral solution with water; this may be preserved for a considerable time, although the solid salt decomposes at the ordinary temperature, in the course of about 48 hours, into nitrogen and diiodochlorobenzene. *Trichlorodiazobenzene chloride* forms colourless prisms, and its aqueous solution is neutral. When the solid substance is exposed to sunlight, it decomposes into nitrogen and tetrachlorobenzene; this decomposition only proceeds very slowly in the dark. *Tribromodiazobenzene bromide* behaves in a precisely similar manner. With well-cooled aqueous potassium iodide, the diazobenzene salts give precipitates which probably consist of the corresponding iodides, although it has been found impossible to isolate them in the pure state. *Diiododiazobenzene iodide* is thus formed as a red, microcrystalline precipitate, which explodes in the dry state when touched. A solution of diiododiazobenzene chloride in water is quite stable, but, when potassium iodide is added, the diazo-iodide is precipitated, and at once decomposes quantitatively into nitrogen and triiodobenzene.

The aqueous solutions of these halogen-substituted diazo-salts, on the other hand, are remarkably stable. Trichlorodiazobenzene chloride, for example, may be boiled with water, or even with a mixture of hydrochloric and nitric acids, without undergoing any alteration, although the solution gives all the other typical diazo-reactions. This is to be explained, according to the author, by the supposition that the syn-diazo-salt, when dissolved in water, combines with a molecule of water and passes into the compound $\begin{matrix}\mathrm{Ph{\cdot}N}\\ \|\\ \mathrm{HO{\cdot}N,HCl}\end{matrix}$, which may therefore be called the hydrochloride of syn-diazobenzene hydroxide.

On boiling with water, the hydrochloric acid is removed, and the typical syn-diazo-decomposition takes place, nitrogen being evolved and phenol formed. From this compound are also formed the various primary unstable syn-derivatives, which are all produced in the presence of alkaline substances, by which the hydrochloric acid is removed. A. H.

Diazo-compounds. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 826—837).—In the change of an isodiazo-compound, OH·N:NR, into one of the normal constitution, N:NR·OH, in the presence of sulphuric acid, nitrous acid is liberated, and can be detected by blowing a current of air through the solution in which the change is going on, and then through an acid solution of potassium iodide and starch. It is therefore probable that the change consists in the decomposition of the isodiazo-hydroxide into a base and nitrous acid, which then react in the presence of acid to form the normal diazo-salt. Nitrous acid was detected in this way with paranitroisodiazobenzene, isodiazobenzene, orthonitroisodiazobenzene, and metanitroparaisodiazotoluene.

It appears that the isodiazo-hydroxide, which contains triad nitrogen, is produced when a free base (containing triad nitrogen) is acted on by nitrous acid; usually, this at once combines with a second mole-

cule of the base to form a diazoamido-compound. When the base is present as a salt, containing pentad nitrogen, the normal diazo-salt, which also contains pentad nitrogen, is produced.

The constitution of the diazo-ethers must be considered as still doubtful.

Griess appears to have had both isodiazo-compounds and bisdiazoamido-compounds under his observation during his researches on the diazo-compounds. The substance described by Griess as parabromodiazobenzene potassium is, in reality, the iso-salt, and, when it is oxidised with potassium ferricyanide, yields parabromodiazobenzolic acid. The "diazobromobenzene," obtained by Griess from the potassium salt by the action of acetic acid, is the free isobromodiazobenzene hydroxide, and was considered by Griess to be identical with another substance which he obtained by the action of dilute aqueous potash on parabromodiazobenzene nitrate solution. The product of this last reaction is, in reality, bisparabromodiazobenzeneparabromanilide, $C_6H_4Br{\cdot}N_2{\cdot}NC_6H_4Br{\cdot}N_2{\cdot}C_6H_4Br$.

The power of preventing or greatly diminishing the formation of colouring matters from normal diazo-compounds, phenols, &c., which is possessed by strong acids, is shared by concentrated alkalis. In both cases the formation of colouring matter proceeds as usual after dilution.

The author also replies to the criticism of Hantzsch (this vol., i, 349), explaining that, in his view, the so-called "ring" diazo-compounds, of the type $C_6H_4<\begin{matrix}N{:}N\\SO_2\end{matrix}>O$, must now be considered to have the "normal" structure, $C_6H_4<\begin{matrix}N{:}N\\ \\SO_2\end{matrix}>O$.

A. H.

Isomerism in the Azo-series. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 837—854).—Numerous diazoamido-compounds have been prepared from the normal- and iso-diazo-derivatives, and in every case it has been found that the two products are identical. Paranitrodiazoamidobenzene has been previously described. *Paranitrodiazoamidotoluene* melts at 158·5—161·5° and crystallises from alcohol in two distinct forms, thick, garnet-red, lustrous prisms, or slender, golden-yellow, silky needles. Both of these forms melt at the same temperature, and can be converted the one into the other by recrystallisation. *Paranitrodiazoamidomesitylene* crystallises in golden-yellow, silky needles, and melts at 135—136° when rapidly heated, at 133° when slowly heated. *Paranitrodiphenylbuzylene*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NH{\cdot}NHPh$, is obtained by the action of phenylhydrazine on paranitrodiazo- or paranitroisodiazo-benzene nitrate, and crystallises from alcohol in dark, reddish-brown needles, but from light petroleum in small, orange-yellow needles, both forms melting at 104·5° (compare Curtius, Abstr., 1893, i, 463).

Paranitrodiazoamidopiperidine has been previously described. The first product of the action of piperidine on the isodiazo-compound is the *piperidine salt* of *paranitroisodiazobenzene hydroxide*, which crystallises in lemon-yellow plates, and melts and decomposes at 102—103°.

In the azo-series, the relations are not quite so simple. Paranitrophenylazo-α-naphthylamine and paranitrophenylazodimethylaniline, which have been previously described, may be prepared either from the normal- or iso-diazo-compound. *Paranitrophenylazodiethylaniline* crystallises from benzene in dark, steel-blue, lustrous needles, and from alcohol in reddish-brown plates with a bronze lustre; both forms melt at 151°. *Paranitrophenylazodimethylorthotoluidine*, prepared from the normal compound, crystallises in brownish-red plates with a bronze lustre, and melts at 121—122°. It has not yet been found possible to prepare a crystalline colouring matter from paranitroisodiazobenzene hydroxide. Paranitrophenylazomonomethylaniline, prepared from the normal diazo-salt (Abstr., 1888, 271), forms orange-red needles or plates, melting at 133°. When prepared from paranitroisodiazobenzene hydroxide, however, the crystals, although identical in every other respect with those of the compound obtained from the normal diazo-salt, differ by having a golden-yellow colour. The two forms retain their characteristic colours on recrystallisation, but the orange-red compound yields a yellow product when it is dissolved in hydrochloric acid, the hydrochloride separated and decomposed by ice-cold ammonia, and the red, flocculent precipitate recrystallised three times. The nature of the relation between the two forms has not yet been ascertained. *Paranitrophenylazoethylaniline* exhibits similar relations. The colouring matter from the normal diazo-salt melts at 114—115° and crystallises in orange-red, lustrous needles, whilst the derivative of the isodiazo-compound forms golden-yellow needles of the same melting point. Paranitrophenylazophenol has been previously described, and may be obtained either from the normal- or the iso-diazo-compound.

The same is true of *paranitrophenylazo-orthocresol*, which forms yellowish-brown clusters melting at 200—201°, and of *paranitrophenylazometacresol*, which crystallises from toluene in violet-brown needles, with a bronze lustre, and from alcohol in long, orange-red, matted needles, melting at 162·5—163·5°.

α-Naphthol yields a mixture of two isomeric derivatives, both with the normal- and the iso-diazo-compound of paranitraniline. The *α-compound* crystallises in dark brownish-red needles, which have a very pronounced, steel-blue, surface lustre; it melts at 277—279°, and decomposes at about 290°. The *sodium* salt forms greenish-brown needles with a bronze lustre. The isomeric *β-compound* forms long, brick-red, matted needles, which have a green, metallic lustre; it melts at 234—235° and decomposes at 255—260°. It is more soluble than the α-compound in boiling amylic alcohol or xylene, by means of which the two forms may be separated. The *sodium* salt crystallises in greenish-black, matted needles. The α-compound is always the chief product when the normal nitrodiazobenzene salt is used, whilst the proportion of the two forms obtained from the isodiazo-compound depends on the solvent employed, alcohol favouring the formation of the α-compound, benzene that of the β-compound. Attempts to convert one of the compounds into the other have, so far, failed. The two compounds yield distinct acetates when heated with acetic

anhydride or chloride. The *α-acetate* melts at 165—166°, and crystallises in ruby-red needles with a steel-blue surface lustre. The *β-acetate* crystallises in brick-red needles and melts at 179·5°.

The two isomeric compounds may also be prepared from paranitrodiazobenzene methyl ether, the *β*-compound being exclusively formed when benzene is used as the solvent, whilst, when alcohol is employed, the product consists entirely of the *α*-compound.

β-Naphthol only yields one azo-compound when treated either with the normal or the iso-diazo-derivative of paranitraniline. Similar isomeric derivatives have also been obtained from *α*-naphthol by the action of the diazo-derivatives of paranitro-orthotoluidine. The *α-compound* forms violet-brown needles, with a steel-blue surface lustre, melts indefinitely, and decomposes sharply at 247°. The *acetate* crystallises in dull, brown needles, melting at 163°. The *β-compound* forms dark brick-red, silky needles, and melts at 245°. When pressed on a porous plate, it exhibits a green, metallic lustre. The *β-acetate* crystallises in brick-red, lustrous needles melting at 172—173°.

A. H.

Parethoxyazobenzene. By Ernest Naegeli (*Bull. Soc. Chim.*, 1894, [3], **11**, 897—898).—Parahydroxyazobenzene is heated with sodium ethoxide in alcoholic solution, and the solution of the sodium derivative thus formed boiled with ethylic iodide for some hours. On removing the solvent, a quantitative yield of *parethoxyazobenzene*, $OEt{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_5$, is obtained in very long, orange needles, having a violet lustre; it melts at 85°, and boils at 325—326°. Jn. W.

Halogen Benzeneazophenols. By John T. Hewitt (*Ber.*, 1895, **28**, 799—803).—The yellow 1 : 2- and the violet 1 : 3-chlorobenzeneazophenols previously described (Abstr., 1894, i, 123) are not isomerides of the red and yellow varieties, but owe their different colour to the fact that they are crystallised with $\frac{1}{2}H_2O$. From 1 : 2-chlorobenzeneazophenol, the following derivatives were prepared (the numbers are melting points); *benzenesulphonate*, yellow prisms, 74°; *barium salt*, yellow needles, with $4H_2O$; and the yellow *mononitroderivative*, 158°. From 1 : 3-chlorobenzeneazophenol were prepared the *benzenesulphonate*, yellow prisms, 97°, and the *barium salt*, orange needles, with $4H_2O$.

1 : 3-*Bromobenzeneazophenol*, $C_6H_4Br{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, is obtained by treating 1 : 3-bromodiazobenzene hydrochloride with an alkaline solution of phenol; it crystallises from alcohol in yellow plates, from water in dark violet plates (containing $\frac{1}{2}H_2O$). Derivatives: *acetate*, lustrous yellow plates, 112°; *benzoate*, orange needles, 122°; *sulphonate*, orange plates, 95°; *barium salt*, yellow needles, with $4H_2O$.

1 : 3-*Chlorobenzeneazosalicylic acid* is obtained by treating 1 : 3-chlorodiazobenzene hydrochloride with an alkaline solution of salicylic acid; it forms yellow spherical crystalline aggregates, melts at 220—221°, and has no tendency to crystallise with water. C. F. B.

Action of Orthonitrobenzylic Chloride on Unsymmetrical Hydrazines. By Carl Paal and Franz Fritz (*Ber.*, 1895, **28**,

931—933; compare C. Paal and A. Bodewig, Abstr., 1892, 1455).—By acetylating compounds of the type $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot NR_2$, the authors hoped to obtain derivatives which would condense to ring compounds of the type $\begin{matrix} N{=}CR_2 \\ | \\ C_6H_4 \cdot CH_2 \end{matrix} > N \cdot NR_2$, but the basic properties of the open chain compounds proved too feeble.

Orthonitrobenzyldiphenylhydrazine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot NPh_2$, from orthonitrobenzylic chloride and unsymmetrical diphenylhydrazine, crystallises from alcohol in red needles, and melts at 143°. It has no basic properties.

On attempting to prepare the corresponding methylphenylhydrazine derivative, the only product obtained was a very small amount of *orthonitrobenzylmethylaniline*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMePh$, which was probably formed from methylaniline, produced by oxidation of unchanged methylphenylhydrazine, as an identical compound was prepared from the former base. Orthonitrobenzylmethylaniline crystallises in large, resplendent, red needles; it melts at 72°, and decomposes when distilled. It is only slightly basic, but, on reduction, yields an unstable, oily base, probably the corresponding amido-compound. Jn. W.

αβ-Diformylphenylhydrazine and αβ-Formylacetylphenylhydrazine. By Martin Freund and Fritz Horst (*Ber.*, 1895, **28**, 944—945).—*αβ-Diformylphenylhydrazine*, is obtained by heating a mixture of phenylhydrazine and formic acid for seven hours. It crystallises from ether to which alcohol has been added, and melts at 126°. It is feebly acid in character, and is precipitated unchanged from the solution in dilute alkalis; it dissolves readily in cold formic acid, in hot water, and in warm, dilute alcohol, but is only sparingly soluble in cold water, ether, or benzene. When distilled, it undergoes decomposition, carbonic oxide, aniline, phenylic isocyanide, and β-formylphenylhydrazine being produced; the last-named substance is also formed when the diformyl derivative is treated with hot, aqueous ammonia.

αβ-Formylacetylphenylhydrazine is obtained from αβ diformylphenylhydrazine by treatment with boiling acetic anhydride; it melts at 86°, and separates from hot water in long, colourless crystals containing water, but this is lost in the desiccator. This compound yields carbonic oxide when heated; the action of hot, aqueous soda gives rise to β-acetylphenylhydrazine. M. O. F.

Action of Hydrazine Hydrate on Phthalic and Maleïc Anhydrides. By Theodor Curtius and Hans A. Foersterling (*J. pr. Chem.*, 1895, [2], **51**, 371—398).—*Phthalylhydrazide*,

$$C_6H_4 < \begin{matrix} CO \cdot NH \\ | \\ CO \cdot NH \end{matrix},$$

is prepared by adding hydrazine hydrate (1 mol.) to phthalic anhydride (1 mol.) dissolved in alcohol; the powder which separates is evaporated several times with water, and in this way the several compounds of which it consists are converted into the hydrazide. It crystal-

lises in slender, colourless needles, does not melt at 340°, can be sublimed at 200°, and distils at higher temperatures. One litre of boiling water dissolves 1 gram of it, and boiling alcohol dissolves it to some extent; otherwise it is insoluble. Its aqueous solution is acid, and it behaves as a monobasic acid, yielding easily soluble alkali salts, the solutions of which give precipitates with the salts of most of the heavy metals. The *potassium*, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NK\end{matrix} + 4H_2O$, *sodium*, *silver*, *barium*, $(C_8H_5O_2N_2)_2Ba + 2H_2O$, and *calcium* derivatives are described. Phthalylhydrazide yields no derivative with benzaldehyde, and neither acids nor alkalis eliminate hydrazine from it; strong acids decompose it with formation of phthalic acid; bromine is without action on it. These facts show that the compound is not a hydrazine, as, indeed, is also evident from the fact that v. Rothenburg has prepared a hydrazine of this formula (Abstr., 1894, i, 285), and finds that it melts at 250°. The substance might contain the group $<\begin{matrix}NH\\ |\\ NH\end{matrix}$ in place of one of the carbonyl-oxygen atoms of phthalic anhydride, but this possibility is negatived, since it yields no azo-compound on treatment with mercuric oxide, and does not split up with evolution of nitrogen and formation of phthalide when heated (compare Abstr., 1891, 1355).

Diacetylphthalylhydrazide, $C_6H_4<\begin{matrix}CO\cdot N\cdot COMe\\ |\\ CO\cdot N\cdot COMe\end{matrix}$, is obtained when phthalylhydrazide is heated with excess of acetic anhydride; it forms crystals which melt at 114°.

Methylphthalylhydrazide, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NMe\end{matrix}$, from the silver derivative and methylic iodide, melts at 235°.

Ethylic phthalylhydrazide-acetate, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot N\cdot CH_2\cdot COOEt\end{matrix}$, is prepared by heating the anhydrous potassium derivative with ethylic chloracetate at 160°; it crystallises in slender, yellowish needles, melts above 300°, and is sparingly soluble in hot water and alcohol. The corresponding *acid* closely resembles the ethylic salt, and may be regarded as a derivative of the still unknown hydrazineacetic acid (see this vol., i, 332), but attempts to isolate the latter from it have failed. The *ammonium* salt is described.

When an excess of hydrazine hydrate (2 mols.) is used in the preparation of phthalylhydrazide, *hydrazine phthalylhydrazide*, $C_6H_4<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot N\cdot N_2H_5\end{matrix}$, is produced; this is a colourless, crystalline powder (sometimes with $4H_2O$), and melts above 270°; being a hydrazine salt, it yields benzylideneazine and phthalylhydrazide when its aqueous solution is shaken with benzaldehyde. Phenylhydrazine is without action on phthalylhydrazide.

Oxidising agents convert phthalylhydrazide into nitrogen and phthalic acid; reducing agents scarcely attack it.

Several compounds are formed when hydrazine hydrate and maleïc

anhydride interact; after many recrystallisations, two, namely, *n*-amidomaleïmide, and maleylhydrazide, were isolated in a pure condition.

n-*Amidomaleïmide*, $CO<^{C_2H_2}_{-O-}>C{:}N{\cdot}NH_2$, is a white powder which melts at 111°, and is insoluble in absolute alcohol, ether, and chloroform, but dissolves freely in water, from which, however, it cannot be recrystallised, for it yields a syrup when evaporated. The *silver* and *copper* derivatives were obtained as precipitates. When an aqueous solution of the imide is shaken with a few drops of benzaldehyde, crystals of a compound which has the properties of benzylideneazine separate, but no hydrazine is eliminated from the imide when it is heated with acetone for six hours.

Acetylamidomaleïmide, $CO<^{C_2H_2}_{-O-}>C{:}N{\cdot}NHAc$, crystallises when the imide is evaporated with glacial acetic acid on the water bath; it forms colourless needles, melts about 280°, and dissolves in water, alcohol, and glacial acetic acid. Methylic iodide has no action on amidomaleïmide.

Maleylhydrazide, $C_2H_2<^{CO{\cdot}NH}_{CO{\cdot}NH}$, forms small, white crystals, melts above 250°, and dissolves sparingly in hot alcohol, but more freely in hot water and glacial acetic acid. Its aqueous solution is strongly acid, and it closely resembles phthalylhydrazide in its behaviour to reagents.

Hydrazine maleate, $COOH{\cdot}C_2H_2{\cdot}COO{\cdot}N_2H_5 + H_2O$ (compare Abstr., 1894, i, 348), is formed by the interaction of maleïc acid (1 mol.) with hydrazine hydrate (1 mol.) in alcohol. It is a loose, white powder, melts at 127°, and is very soluble in water, giving an acid solution. Its conversion into 3 : 5 : 5-trimethylpyrazoline maleate, $C_3H_3N_2Me_3,C_2H_2(COOH)_2$, has been already described (*loc. cit.*).

Hydrazine fumarate, $COOH{\cdot}C_2H_2{\cdot}COO{\cdot}N_2H_5 + 3H_2O$, prepared in a similar manner, crystallises in small white needles; it melts at 157°, and dissolves readily in water, giving an acid solution, which yields a white precipitate with silver nitrate. It is not converted into trimethylpyrazoline fumarate when heated with acetone (compare *loc. cit.*). A. G. B.

Symmetrical Trimethylbenzaldoxime. By Arthur Hantzsch and A. Lucas (*Ber.*, 1895, **28**, 744—753).—Trimethylbenzantialdoxime, $^{C_6H_2Me_3{\cdot}C{\cdot}H}_{HO{\cdot}N}{\!\!\!

the anti-compound from which it is prepared by the action of hydrogen chloride; the anti-aldoxime hydrogen chloride is first formed, then the syn-compound, and by the further action of the gas a mixture of both; this regeneration of the anti-aldoxime is probably due to the presence of a little moisture. The compound crystallises in slender, colourless needles, melts at 179°, is more sparingly soluble than the anti-aldoxime, and yields no acetate. It is not altered when boiled with water, but with soda yields trimethylbenzonitrile which boils at 235—238°, not 225—230°, as stated by Küster and Stallberg (Abstr., 1894, i, 278). This is the first synaldoxime which has yielded a nitrile directly without previous conversion into the acetate. Phosphorus pentachloride converts aromatic oximes into nitriles, aliphatic oximes yield amides, trimethylbenzosynaldoxime yields the nitrile, but the anti-aldoxime gives some nitrile, the remainder undergoing intramolecular rearrangement (Beckmann's reaction) and yielding formylmesidide, dimolecular formylmesidide, and polymolecular formylmesidide.

Formylmesidide, $C_6H_2Me_3{\cdot}NH{\cdot}CHO$, is formed in larger quantity at low temperatures when excess of the chloride is avoided; it is readily soluble in hot water, melts at 176°, and, by the action of hydrochloric acid, is resolved into formic acid and mesidine from which it is readily prepared. *Dimolecular formylmesidide chloride*,

$$C_6H_2Me_3{\cdot}N<\begin{matrix}CHCl\\CHCl\end{matrix}>N{\cdot}C_6H_2Me_3,$$

or $C_6H_2Me_3{\cdot}NH{\cdot}CCl{:}CCl{\cdot}NH{\cdot}C_6H_2Me_3$, occurs together with the preceding compound from which it is readily prepared by the action of phosphorus pentachloride; it crystallises in lemon-yellow needles, melts at 178°, and is practically unaffected by boiling with water, ammonia, alkalis, or dilute acids. Its constitution is probably represented by the first of the above formulæ, as it is comparatively readily converted into formic acid and mesidine. *Dimolecular formylmesidide*, $C_6H_2Me_3{\cdot}N<\begin{matrix}CH(OH)\\CH(OH)\end{matrix}>N{\cdot}C_6H_2Me_3$, is prepared by boiling the preceding compound with alcohol, or by the action of concentrated sulphuric acid at ordinary temperatures; it melts at 285°, sublimes at higher temperatures, is very sparingly soluble, not acted on by aqueous or alcoholic acids and alkalis at 100°, but with concentrated hydrochloric acid at 200° it yields mesidine and formic acid. Its molecular weight and that of the chloride were determined by the cryoscopic method in benzene and phenol solution respectively. *Polymolecular formylmesidide* was only obtained in small quantity and was separated from the above chloride by taking advantage of its insolubility in benzene; it sublimes without melting, and is more stable and less soluble than the preceding compound, with which it is polymeric or isomeric, as it yields the same products when hydrolysed.

J. B. T.

Action of Acetanilide on Mercuric Acetate. By Leone Pesci (*Gazzetta*, 1894, **24**, ii, 449—452).—*Paramercuriodiphenylenediacetylmercuriodiammonium acetate*, $Hg<\begin{matrix}C_6H_4{\cdot}NHAc\\C_6H_4{\cdot}NHAc\end{matrix}Hg(C_2H_3O_2)_2$, is pre-

pared by gradually adding mercuric acetate to a boiling aqueous solution of acetanilide and heating the solution until caustic potash gives a pure white precipitate; the salt, which separates on cooling, crystallises in lustrous rhombs melting at 218—220°. The corresponding *chloride* crystallises with $2H_2O$ in colourless needles melting at 256°, whilst the *sulphate* forms colourless needles or laminæ which, on heating, decompose without melting. The *hydroxide* is a micro-crystalline substance having a strongly alkaline reaction; it decomposes at 270°, and when treated with sodium sulphide or barium sulphide loses mercury yielding *paramercurioacetanilide*, $Hg(C_6H_4{\cdot}NHAc)_2$. This substance crystallises in colourless, flexible needles melting at 244—246°, and when heated with alcoholic potash in a closed tube yields paramercurioaniline, showing that in the above compounds the mercury occupies the para-position relatively to the amidogen residue in the aromatic nucleus. W. J. P.

Mercurioacetanilides. By Antonio Piccinini (*Gazzetta*, 1894, **24**, ii, 453—457).—The mercurioacetanilide prepared by Pesci (see preceding abstract) is isomeric with the substance obtained by Oppenheim and Pfaff (*Ber.*, 1874, **7**, 624) by the action of yellow mercuric oxide on fused acetanilide, to which the constitution $Hg(NAcPh)_2$ was assigned. The latter substance is decomposed by sodium thiosulphate, potassium iodide, or ammonium bromide, yielding acetanilide in accordance with the general reactions of mercurammonium compounds; Pesci's compound, on the other hand, is not changed by these reagents. W. J. P.

Organo-mercuric Compounds derived from Aniline. By Antonio Piccinini (*Gazzetta*, 1894, **24**, ii, 457—465).—Paramercuriodiphenylenemercuriodiammonium acetate is converted into paramercurioaniline by sodium thiosulphate; whilst if warmed with potassium iodide solution, it yields *paramercurioaniline iodide*, $NH_2{\cdot}C_6H_4{\cdot}HgI$, probably as a product of the action of mercuric iodide on paramercurioaniline produced in the first stage of the action. The iodide crystallises in colourless laminæ melting and decomposing at 165°. The corresponding *bromide*, $NH_2{\cdot}C_6H_4{\cdot}HgBr$, is formed by the action of ammonium bromide on the acetate mentioned above; it crystallises in colourless laminæ melting at 182°.

Paramercuriodiphenylenedimethylmercuriodiammonium acetate is converted into paramercuriomethylaniline by sodium thiosulphate, and into *paramercuriomethylaniline bromide* by ammonium bromide; this salt crystallises in colourless needles melting and decomposing at 164°.

Paramercuriodiphenylenetetramethylmercuriodiammonium acetate gives mercuriodimethylaniline with sodium thiosulphate and the *iodide* $NMe_2{\cdot}C_6H_4{\cdot}HgI$ of the latter base with potassium iodide; the iodide crystallises in needles or scales melting and decomposing at 174—195°. The corresponding *bromide* is obtained by acting on the acetate of the substituted ammonium with ammonium bromide; it crystallises in lustrous, colourless scales melting and decomposing at 195°.

Paramercuriodiphenylenediethylmercuriodiammonium acetate is converted into mercurioethylaniline by sodium thiosulphate, and by potassium iodide into the *iodide* $NHEt{\cdot}C_6H_4{\cdot}HgI$, crystallising in colourless needles melting at 137°.

Paramercuriodiphenylenetetrethylmercuriodiammonium acetate, under similar conditions, yields paramercuriodiethylaniline; its *iodide*, $NEt_2{\cdot}C_6H_4{\cdot}HgI$, crystallises in colourless needles melting at 120°, and its *bromide* in colourless needles melting at 154·5°.

All these ammonium derivatives thus behave in a similar and characteristic manner with sodium thiosulphate, potassium iodide and ammonium bromide respectively. W. J. P.

Paramercuriodiethylaniline. By Pio Pigorini (*Gazzetta*, 1894, **24**, ii, 465—468).—*Mercuriodiethylaniline chloride*, $NEt_2{\cdot}C_6H_4{\cdot}HgCl$, is obtained from paramercuriodiethylaniline by the process used by Michaelis and Rabinerson (Abstr., 1890, 1269) in preparing mercuriodimethylaniline chloride; it crystallises in colourless needles melting at 164°. On heating with sodium carbonate solution, it yields the *oxide* $O(Hg{\cdot}C_6H_4{\cdot}NEt_2)_2$; this is a substance having a strongly alkaline reaction and crystallises in lustrous, colourless needles melting at 220°; it yields paramercuriodiethylaniline on treatment with sodium thiosulphate. W. J. P.

Paraphenetoïlcarbamide, "Dulcin." By Ludwig Wenghöffer (*Chem. Centr.*, 1894, i, 771—773; from *Apoth. Ztg.*, **9**, 200—202). —*Paraphenetoïlcarbamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$, is obtained by gradually adding a solution of paraphenetidine in benzene or toluene to a 20 per cent. solution of carbonyl chloride in benzene or toluene, whereby paraphenetidinecarbonyl chloride, $Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$, is formed; after remaining from half an hour to one hour, the mixture is filtered and the filtrate treated with ammonia gas or shaken with a strong solution of ammonia. The ammonium chloride which is precipitated is filtered off and the filtrate evaporated; the residue is washed with cold water and crystallised from boiling water. If concentrated solutions are employed in the above reaction, diparaphenetoïlcarbamide, $CO(NH{\cdot}C_6H_4{\cdot}OEt)_2$, is also formed. According to F. v. Heyden, when large quantities of the above reagents are employed, paraphenetidinecarbonyl chloride is not formed, or only in small quantities; but the reaction takes place with the formation of paraethoxyphenylic isocyanate, $CO{:}N{\cdot}C_6H_4{\cdot}OEt$, which when treated with ammonia yields paraphenetoïlcarbamide.

Paraethoxyphenylic isocyanate is easily obtained by passing carbonyl chloride over melted paraphenetidine hydrochloride, or by heating paraphenetidine with carbonyl chloride at 230°. It is also obtained by passing carbonyl chloride over diparaphenetoïlcarbamide heated at 230°.

Paraphenetoïlcarbamide is obtained in small quantities by the action of carbamide on paraphenetidine. A good yield is, however, obtained when paraphenetidine hydrochloride is fused with carbamide; at the same time, when excess of carbamide is employed, diparaphenetoïlcarbamide is formed, which, however, is easily converted

into paraphenetoïlcarbamide by heating it with an equivalent quantity of carbamide in a closed vessel at 150—160°.

Paraphenetoïlcarbamide is likewise obtained by heating paraphenetidine with acetylcarbamide, carbamine chloride or urethane. It forms colourless crystals, melts at 173—174°, is soluble in 800 parts of water at 15°, in 50 parts of boiling water, and in 25 parts of 90 per cent. alcohol. When boiled with water, it is gradually decomposed into diparaphenetoïlcarbamide and ammonium carbonate. It dissolves completely and without any coloration in concentrated sulphuric acid, and has no injurious action on the animal organism. It can be detected by the following reaction: a small quantity is boiled with two or three drops of pure carbolic acid and sulphuric acid, then somewhat diluted with water, and to the cold solution a solution of sodium hydroxide or ammonia is added, when a blue coloration is formed at the junction of the two liquids.

E. C. R.

Benzanilide. By Ernest Naegeli (*Bull. Soc. Chim.*, 1894, [3], **11**, 891—893).—Improved methods of preparation. Benzoic chloride is added to excess of aniline (10 mols.) at 30—40°, and the mixture heated at 60—70° for half an hour. The excess of aniline is then dissolved out with dilute hydrochloric acid, leaving a quantitative yield of an almost white product.

A 90 per cent. yield of a less pure product may be obtained from the acid. This is melted in a retort, and the aniline (1 mol.), heated to about the same temperature, added; the temperature is then repeatedly raised from 180° to 225° during about 30 hours, the loss of aniline being made up from time to time. The cold product, after washing with dilute alkali and acid, is fairly pure; the colour, however, is violet-grey, and the alcoholic solution shows a strong violet-brown fluorescence. Further purification may be effected by sublimation.

Jn. W.

Action of Phthalic Chloride on Nitranilines. By N. Dobreff (*Ber.*, 1895, **28**, 939—941; compare Pawlewski, this vol., i, 134).—Paranitrophthalanil is obtained by heating paranitraniline with phthalic chloride; it crystallises from alcohol in yellowish needles and melts at 190—190·5° (compare *loc. cit.*). The solution in alkalis and alkali carbonates is yellow. Metanitrophthalanil crystallises from alcohol and melts at 236—236·5°.

M. O. F.

Phenyl Derivatives of Glycolaldehyde. By Cæsar Pomeranz (*Monatsh.*, 1894, **15**, 739—746).—The acetal of the phenyl derivative of glycolaldehyde, *phenoxyacetal*, $OPh{\cdot}CH_2{\cdot}CH(OEt)_2$, is obtained on heating an alcoholic solution of sodium phenoxide and monochloracetal for eight hours at 200°. It boils at 257°, and when heated with dilute sulphuric acid and subsequently distilled in a current of steam, forms the hydrate of the phenyl derivative of glycolaldehyde, *phenoxyacetaldehyde*, $OPh{\cdot}CH_2{\cdot}COH + H_2O$. This melts at 38°, has an aromatic odour, reduces silver solution, is converted by silver oxide

into phenoxyacetic acid, and, on distillation under reduced pressure, loses water and yields the aldehyde; this boils at 118—119° (30 mm.), and after remaining some days changes to a jelly-like mass. It yields a *hydrazone*, $C_{14}H_{14}N_2O$, which crystallises from alcohol in bright, yellow prisms and melts at 86°. The corresponding *oxime*, $C_8H_9O_2N$, crystallises from light petroleum in prisms, melts at 95°, and when warmed with acetic anhydride yields *phenoxyacetonitrile*, $OPh{\cdot}CH_2{\cdot}CN$, which boils at 239—240°. G. T. M.

β-Halogenised Ketones. By HANS RUPE and FELIX SCHNEIDER (*Ber.*, 1895, **28**, 957—966).—β-Chloro-ω-benzylacetophenone,

$$CHPhCl{\cdot}CH_2{\cdot}COPh,$$

was first obtained by Claisen and Claparède on submitting a mixture of benzaldehyde with acetophenone to the action of hydrogen chloride. When it is heated with phenylhydrazine (2 mols.), triphenylpyrazoline is formed. The *bromo*-derivative crystallises in nacreous leaflets and melts at 111°.

β-Thiocyano-ω-benzylacetophenone, $SNC{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, is obtained by heating an alcoholic solution of the chloro-ketone for several hours with potassium thiocyanate. It melts at 88—89°, and undergoes no change when heated on the water bath; the solutions in organic solvents exhibit a bright blue fluorescence. Unlike most compounds of this class, it does not yield a hydroxythiazole derivative under the influence of condensing agents. When heated with phenylhydrazine, it gives rise to triphenylpyrazoline.

β-Cyano-ω-benzylacetophenone, or *α-phenyl-β-benzoylpropionitrile*, $CN{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, which melts at 127°, is prepared by heating an alcoholic solution of the chloro-ketone with potassium cyanide for half an hour in a reflux apparatus; if the liquid is cooled immediately after the first separation of potassium chloride, benzylideneacetophenone is the chief product. A *compound*, $C_{31}H_{24}NO$, is also formed in varying quantity; it dissolves with difficulty in most solvents, but crystallises from boiling glacial acetic acid in slender, white needles and melts at 249°.

α-Phenyl-β-benzoylpropionic acid crystallises from alcohol in white needles and melts at 153°. The *methylic* salt melts at 104°, the *ethylic* salt at 37—38°, and the *amide* at 149°. The *anhydride* of the phenylhydrazone, $C_{22}H_{18}N_2O$, crystallises from ether in stellar aggregates, and melts at 122—123°.

Chlorobenzylacetophenone yields a *compound* which melts at 155° when heated with aniline; paratoluidine gives rise to a *compound*, $C_6H_4Me{\cdot}NH{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, which melts at 166·5°, and forms a *bromo*-derivative melting at 100·5°.

Benzylideneacetophenoneoxime crystallises in white needles and melts at 107—108°; the *bromo*-derivative melts at 152°. An isomeride is formed when the alcoholic solution of β-chloro-ω-benzylacetophenone is heated with aqueous hydroxylamine for an hour and a half on the water bath; it crystallises in white needles and melts at 73°. It does not form a bromo-derivative, and it also differs from the isomeric substance in its behaviour towards hot, dilute acids, which are with-

out action on it. This is due to the fact that 1 mol. of hydrogen chloride has been removed from the oxime of β-chloro-ω-benzylacetophenone, giving rise to *diphenyldihydroisoxazole*, $CHPh<^{O\cdot N}_{CH_2}>CPh$ (compare Abstr., 1892, 992). A *compound*, which melts at 190°, is formed at the same time; it yields a *bromo*-derivative which melts at 95°. M. O. F.

Thio-Derivatives of Ketones. By EUGEN BAUMANN and EMIL FROMM (*Ber.*, 1895, **28**, 895—907).—It has been previously shown (*Ber.*, **22**, 1035 and 2592) that acetone and hydrogen sulphide only react in presence of some condensing agent such as hydrogen chloride or zinc chloride; ethyl methyl ketone, diethyl ketone, ethylic acetoacetate, pinacone, acetophenone, methyl hexyl ketone, quindecyl methyl ketone, and metadihydroxybenzophenone all resemble acetone in this respect, but the last three compounds do not react even in presence of a condensing agent. The ketones thus present a marked contrast to the aldehydes, most of which readily combine with hydrogen sulphide. The ketones which react yield only one trithio-derivative instead of the two stereoisomerides which are indicated by theory, and E. Wörner has recently shown that none of the aromatic hydroxy- and benzoylaldehydes form isomeric trithio-compounds, but that the corresponding alkyloxy-aldehydes follow the general rule and yield the two stereoisomerides.

Acetophenone and hydrogen sulphide, in presence of hydrogen chloride, give four compounds—thioacetophenone, trithioacetophenone, anhydrotriacetophenone bisulphide, and a green, resinous compound, containing oxygen and sulphur.

Thioacetophenone, S:CPhMe, is the first product of the action, and is most readily obtained by the rapid distillation of trithioacetophenone; it is also formed in small quantity by the interaction of alcoholic hydrochloric acid and trithioacetophenone at 30—40°; at lower temperatures the reverse change occurs. It is a blue, oily liquid with a smell of garlic; the colour of its vapour resembles that of iodine, it is rapidly decomposed by water, and yields a mixture of cinnamene and ethylbenzene when boiled.

Trithioacetophenone, $S<^{C(MePh)\cdot S}_{C(MePh)\cdot S}>CMePh$, which is most readily formed at 0°, crystallises from alcohol in needles, and melts at 122°. It is not volatile with steam, is not decomposed by alcoholic potash, has no smell, and, in alcoholic solution, is not affected by a trace of iodine. All attempts to prepare an isomeric compound were fruitless. The molecular weight was determined cryoscopically. The principal compound formed by the action of ammonium sulphide on acetophenone in alcoholic solution is not "polymeric thioacetophenone" (m. p. 119·5°), as stated by Engler (*Ber.*, **11**, 930), but *α-phenylethylic bisulphide*, $S_2(CHPhMe)_2$ (compare following abstract).

The residue obtained by the distillation of trithioacetophenone or of thioacetophenone, consists of 2 : 5- and 2 : 4-diphenylthiophen (this vol., i, 337). *Anhydrotriacetophenone bisulphide*, $S<^{C(MePh)—S}_{C(MePh)CH}>CPh$

or $CMePh<^{S}_{S}>CPh\cdot CH\cdot CMePh$, is formed together with the trithio-compound, but is deposited more slowly; it crystallises in needles, melts at 107—108°, and, at 180°, yields thioacetophenone, hydrogen sulphide, and 2 : 4-diphenylthiophen only (*loc. cit.*). It is not formed from trithioacetophenone by the action of alcoholic hydrogen chloride, but is probably derived from labile cis-trithioacetophenone, as indicated by the first formula. The molecular weight was determined in naphthalene solution. The resinous compound is formed during the preparation of trithioacetophenone if the temperature rises or if the solution is too concentrated; when distilled, it yields thioacetophenone, cinnamene, hydrogen sulphide, and 2 : 4-diphenylthiophen only, so that it is probably a mixture of anhydrotriacetophenone bisulphide with acetophenone condensation products. J. B. T.

Action of Ammonium Sulphide on Acetophenone. By EUGEN BAUMANN and EMIL FROMM (*Ber.*, 1895, **28**, 907—914).—Acetophenone reacts like benzophenone with ammonium sulphide in alcoholic (65 per cent.) solution at ordinary temperatures, and yields *α-phenylethylic bisulphide*, $S_2(CHMePh)_2$, not "polymeric thioacetophenone," as stated by Engler; it crystallises in small, colourless prisms, and melts at 57—58°; its molecular weight agrees with the formula, and its constitution is shown by its reduction to *α-phenylethylic mercaptan*, $CHMePh\cdot SH$, which boils at 119—200°, and gives the ordinary mercaptan reactions. The bisulphide, when heated, is readily resolved into cinnamene, a little ethylbenzene, sulphur, and hydrogen sulphide; the residue consists of sulphur, 2 : 5- and 2 : 4-diphenylthiophen (compare this vol., i, 337); the first few drops of the distillate are blue, and contain a trace of thioacetophenone. In addition to the above bisulphide, an oily compound is formed; it is practically free from thioacetophenone, commences to decompose at 160°, and, when further heated, evolves hydrogen sulphide, and yields ethylbenzene and a little cinnamene; the residue contains sulphur, and 2 : 5- and 2 : 4-diphenylthiophen. With stronger alcohol, and operating exactly as Engler describes, crystals of ammonium hydrogen sulphide are deposited; the oil obtained by precipitation with water, yields, when distilled, ethylic sulphide, ethylic alcohol, cinnamene, ethylbenzene, thioacetophenone (traces), acetophenone, 2 : 5- and 2 : 4-diphenylthiophen, sulphur, and hydrogen sulphide; the residue consists of resinous matter and sulphur. In explanation of the difference between these results and Engler's, the authors suggest that his "polymeric thioacetophenone" (m. p. 119°) was 2 : 4-diphenylthiophen; the melting points and general properties agree tolerably well; the difference in composition was probably due to the presence of free sulphur in Engler's compound, which does not greatly affect the melting point, and is extremely difficult to separate. J. B. T.

Diphenylamine-*n*-oxychlorophosphine. By PAUL OTTO (*Ber.*, 1895, **28**, 613—616).—When diphenylamine (1 mol.) is heated for 12 hours at 160° with phosphorus oxychloride (2 mols.) *diphenylamine-n-oxychlorophosphine*, $NPh_2\cdot POCl_2$, is formed. This crystallises in

white plates and melts at 57°. With water, it yields the *phosphinic acid*, $NPh_2{\cdot}PO(OH)_2$, which is itself unstable, but the *ethylic*, *phenylic*, and 1 : 4-*tolylic* salts of which, $NPh_2{\cdot}PO(OEt)_2$, &c., can be obtained respectively by boiling the chlorophosphine with alcohol or heating it with phenol or 1 : 4-cresol in sealed tubes; they are white substances, and melt at 175°, 180°, and 178°. When the chlorophosphine (1 mol.) is heated with aniline, 1 : 2-toluidine, or piperidine (4 mols.), *diphenylaminedianiline*-n-*phosphine oxide*, $NPh_2{\cdot}PO(NHPh)_2$, or the corresponding *di*-1 : 2-*toluidine*, or *dipiperidine*, compounds, are respectively formed; these are white, and melt at 232°, 219°, and 200°.

C. F. B.

1 : 4-Chloraniline-*n*-oxychlorophosphine. By PAUL OTTO (*Ber.*, 1895, **28**, 616—620).—When phosphorous oxychloride (2 mols.) is heated with 1 : 4-chloraniline hydrochloride (1 mol.), 1 : 4-*chloraniline*-n-*oxychlorophosphine*, $C_6H_4Cl{\cdot}NH{\cdot}POCl_2$, is formed; it crystallises in white needles, and melts at 107°. When it is dissolved in ammonia, and the solution acidified with hydrochloric acid, the *phosphinic acid*, $C_6H_4Cl{\cdot}NH{\cdot}PO(OH)_2$, is formed; this crystallises in white, silky needles, and melts at 155°; the colourless *ethylic salt* melts at 76°, the yellowish *phenylic salt* at 117°.

When phosphorus oxychloride (1 mol.) is heated with 1 : 4-chloraniline hydrochloride (2 mols.) a waxy mass is obtained, from which *di*-1 : 4-*chloraniline*-n-*phosphinic acid*, $(C_6H_4Cl{\cdot}NH)_2PO{\cdot}OH$, can be isolated; it crystallises in silvery white plates, and melts at 126°. If the waxy mass is heated over a bare flame, a violent evolution of hydrogen chloride occurs, and *oxyphosphazo*-1 : 4-*chlorobenzenechloranilide*, $C_6H_4Cl{\cdot}NH{\cdot}PO{:}N{\cdot}C_6H_4Cl$, is formed; this crystallises in white needles, and melts above 300°, as does also its yellow *dinitro-derivative*.

When phosphorus oxychloride (1 mol.) is heated with 1 : 4-chloraniline (6 mols.), the *phosphine oxide*, $(C_6H_4Cl{\cdot}NH)_3PO$, is formed; this crystallises in white plates, and melts at 230°; its yellow *trinitro*- and white *tribromo-derivatives* melt respectively at 249° and 236°.

1 : 4-Chloraniline-*n*-oxychlorophosphine reacts with aniline, 1 : 2-toluidine and piperidine, yielding mixed phosphine oxides,

$$C_6H_4Cl{\cdot}NH{\cdot}PO{\cdot}(NHPh)_2, \text{ &c.},$$

which crystallise in white plates, and melt respectively at 115°, 150°, and 175°.

C. F. B.

Nitrobenzoic acids: An omission. By WILLIAM OECHSNER DE CONINCK (*Bull. Soc. Chim.*, 1894, [3], **11**, 717; compare this vol., i, 280).—The nitrobenzoic acids, taken in pairs, bear the same relations to each other as do the amidobenzoic acids.

JN. W.

Derivatives of Cinnamic acid. By LAZAR EDELEANU and A. ZAHARIA (*Chem. Centr.*, 1894, ii, 208—209; from *Bul. Soc. Sci. fizice*, Buckarest, **3**, 80—86).—The following substances have been obtained by agitating amines or phenols with cinnamic chloride in the presence of potash, and crystallising the product from alcohol.

Cinnamoylpariodaniline, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4I$ [1 : 4], melting at 204°, sparingly soluble in alcohol. *Cinnamoylorthotoluidine*, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, melting at 167°. *Cinnamoylparatoluidine*, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, melting at 168°. *Cinnamoylparaxylidine*, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me_2$ [NH : Me_2, 1 : 3 : 4], melting at 175—176°. *Cinnamoylmetaxylidine*, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me_2$ [NH : Me_2, 1 : 3 : 5].

Dibromocinnamic chloride reacts violently with ammonia and with aniline; in the former instance *dibromocinnamamide*,

$$CHPhBr{\cdot}CHBr{\cdot}CO{\cdot}NH_2,$$

is formed; it crystallises from alcohol, in which it is very sparingly soluble, in needles with silky lustre, and melts at 217°. In the latter case, a crystalline substance, readily soluble in alcohol, and dibromocinnamylanilide, melting at 174°, are produced. With methylaniline and dimethylaniline, cinnamic chloride, in alkaline emulsion, yields cinnamic anhydride. Cinnamic chloride does not react with secondary and tertiary amines; with phenols, the action is much less vigorous than with the amines, and it is frequently advantageous to omit the potash with phenols. *Orthotolylic cinnamate*, m. p. 85°, has been obtained from orthocresol, *paratolylic cinnamate*, m. p. 60°, from paracresol and similarly, from catechol, a salt melting at 125°; from resorcinol, a salt melting at 113—114°; from quinol, a salt melting at 186—187°; and from α-naphtol, a salt melting at 111°.

D. A. L.

Thionyl Compounds of some Aromatic Ethylic Salts. By Alfred Herre (*Ber.*, 1895, **28**, 593—600).—These compounds have been prepared by heating ethylic salts of aromatic amido-acids with thionyl chloride in benzene solution. The presence of hydroxyl in the benzene ring hinders the formation of a thionylamine; for example, ethylic amidosalicylate yields no thionylamine; ethylic amidoanisate does, however. Ethylic 1 : 2-amidocinnamate yields carbostyril. The temperatures given below, except where otherwise indicated, are melting points.

Ethylic 4-*amidocinnamate*, yellow needles, 68—69°; the *thionyl derivative*, $SO{:}N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COOEt$, yellow needles or plates, 95°; it boils at 235—240° under 90—100 mm. pressure. *Ethylic* 3 : 5-*nitroamidobenzoate*, prepared by reducing the dinitro-salt with ammonium sulphide, yellow needles, 155°; *thionyl derivative*, lustrous yellow plates, 48—49°. *Methylic* 3 : 5-*dinitrobenzoate*, colourless prisms and plates, 112°; when reduced with ammonium sulphide it yields the *nitramidobenzoate*, yellow needles, 160°; the *thionyl derivative* of the latter, yellow crystals, 55—56°. *Ethylic* 4-*amidotoluate*, by reducing the corresponding nitro-compound with alcoholic ammonium sulphide; colourless needles, 79°; *thionyl derivative*, yellow crystals, 14—15°. *Methylic* 4-*nitrotoluate*, needles, 72°; *amidotoluate*, white prisms, 115°; *thionyl derivative* of the latter, yellow plates, 94°. *Ethylic* 3-*amidosalicylate*, by reducing the nitro-compound with iron and hydrochloric acid, forms white needles which darken when exposed to air, and melts at 145°. *Ethylic thionyl*-3-*amidoanisate*, yellow prisms, melting at 45°.

C. F. B.

Isomerism of Ethylic Formylphenylacetate. By WILHELM WISLICENUS (*Ber.*, 1895, **28**, 767—774).—The isomerism of the two ethylic formylphenylacetates, CHO·CHPh·COOEt, previously described by the author (Abstr., 1887, 129), is similar to that observed by Claisen in the hydroxymethylene- (formyl-) derivatives and the 1 : 3-diketones. Of the dibenzoylacetones, the more acid one reacts with ferric chloride, and is formed from the other by the action of sodium ethoxide. The ethylic formylphenylacetates show the opposite behaviour, the liquid isomeride alone reacts with ferric chloride, is sparingly soluble in alkalis, and is readily converted by them into the solid compound. Both substances appear to yield identical copper salts, and they have the same molecular weight. On the assumption of their tautomerism they have the formulæ CHO·CHPh·COOEt and OH·CH:CPh·COOEt, the latter represents the solid acid compound, the former the liquid isomeride, and their behaviour is in accord with Perkin's observations that the keto-form predominates as the temperature rises. Too little is known of the ferric chloride reaction, for this to serve as an argument against these formulæ. The compounds may be stereoisomeric, $\begin{matrix}H\cdot C\cdot OH\\ \|\\ Ph\cdot C\cdot COOEt\end{matrix}$ and $\begin{matrix}H\cdot C\cdot OH\\ \|\\ COOEt\cdot C\cdot Ph\end{matrix}$; in this case, three substances are possible, but it is probable that only one form might be capable of existence. Each isomeride slowly changes into the other at ordinary temperatures, apparently until equilibrium is established, but the solid is more readily produced at low, the liquid at high, temperatures. With phenylhydrazine in alcoholic or ethereal solution, at ordinary temperatures, both isomerides yield a *phenylhydrazone*, $C_{17}H_{18}N_2O_2$, which is deposited in colourless crystals, melts at 63—64°, gives a dark cherry colour with concentrated sulphuric acid, and a dark brown coloration with ferric chloride. When heated at 180°, or by the action of hydrogen chloride, it is converted into 1 : 4-diphenylpyrazolone (m. p. 195—196°). From the mother liquor, two compounds are deposited in small quantity, the one in yellow prisms, the other in small yellow needles; they contain nitrogen, and melt at 91—93° and 155—156° respectively. The former is probably the *phenylhydrazide*, CHO·CHPh·CO·NH·NHPh.

J. B. T.

Behaviour of the Calcium Salts of Alkyl Derivatives of Aromatic Acids on dry Distillation. By EDUARD HÜBNER (*Monatsh.*, 1894, **15**, 719—738; compare Arnstein, Abstr., 1894, i, 527).—When calcium metamethoxybenzoate is submitted to dry distillation, it yields anisoïl, phenol, and methylic metamethoxybenzoate, which boils at 236—238°. Calcium methylsalicylate gives anisoïl, phenol, methylsalicylic acid and methylic methylsalicylate. β-Creosotic acid (orthohomosalicylic acid) [COOH : OH : Me = 1 : 2 : 3] melts at 163—164°, and forms the following derivatives. A *calcium salt*, which crystallises with $2H_2O$; a *barium salt*, which crystallises with $3H_2O$; a *methylic salt*, which boils at 232—233°; and an *ethylic salt*, which boils at 242—243°. On heating the methylic salt with potash and methylic iodide, the compound $OMe\cdot C_6H_3Me\cdot COOMe$ is formed. It boils at 241—242°, and on hydrolysis yields the acid

$OMe\cdot C_6H_3Me\cdot COOH$,

which melts at 85°, yields a *barium salt*, crystallising with $3\frac{1}{2}H_2O$, and a *calcium salt*, which, on dry distillation, gives orthocresol, the methyl derivative of orthocresol and methylic orthomethoxymetatoluate. Methoxynaphthoic acid [OMe : COOH = α : β] melts at 127°; it is prepared from the methylic salt, which boils at 223—225° (60 mm.). The calcium salt, on dry distillation, yields α-naphthol and the methyl derivative of naphthol, but does not appear to form the methylic salt of naphthoic acid. G. T. M.

Formation of Veratric acid from Hemipinic acid. By CARL KÜHN (*Ber.*, 1895, **28**, 809—811).—*Amidoveratric acid* (dimethoxyanthranilic acid), $NH_2{\cdot}C_6H_2(OMe)_2{\cdot}COOH$, is formed when hemipinimide is treated with alkaline sodium hypochlorite. It crystallises in colourless needles, melts at 181—183°, and is soluble in dilute alkalis and acids. The *hydrochloride* crystallises in needles. The *acetyl*-derivative also forms colourless needles, and melts at 188—190°. When treated with an alcoholic solution of amylic nitrite and sulphuric acid, the free acid is converted into veratric acid, the yield amounting to 43 per cent. A. H.

Glyoxylic acid. By CARL BOETTINGER (*Arch. Pharm.*, 1894, **232**, 704—718; and 1895, **233**, 100—104).—With phenols, glyoxylic acid forms condensation products of, as yet, uncertain constitution. These compounds give precipitates with a solution of gum.

α-Diresorcinolacetic acid, $C_{14}H_{12}O_6$, has already been obtained by Causse, who, however, on insufficient evidence, considered it to have the formula $COOH{\cdot}CH(O{\cdot}C_6H_4{\cdot}OH)_2$. It crystallises in needles which give off vapour at 240° and melt to a clear oil. It yields an *acetyl derivative* melting at 138°, which is probably the triacetyl derivative $C_{14}H_7O_5(C_2H_3O)_3$, but may be a diacetyl derivative.

β-Diresorcinolacetic acid is formed at the same time as the α-compound; it is a brittle, white mass, easily soluble in cold water. Its salts resemble those of the α-acid. It reacts readily in the cold with acetic anhydride, and forms the same acetyl derivative as the α-compound.

β-Dicatecholacetic acid forms a yellow, hygroscopic, glass-like substance. It yields a *triacetyl derivative*.

β-Dipyrogallolacetic acid is very easily obtained. It forms a hygroscopic, white mass, which loses 3 mols. of water at 100°. When an alkali is added to a solution of the acid, a very intense and characteristic blue coloration is produced. It yields a *triacetyl derivative*, $C_{14}H_7O_5(C_2H_3O)_3$, which melts at 123°.

The phloroglucinol derivative was not isolated in a pure state.

The resorcinol and phloroglucinol derivatives give, with bromine, a precipitate which does not redissolve when excess of bromine is added and the liquid heated. With bromine, the catechol derivative gives a precipitate which dissolves in excess of bromine water. The pyrogallol derivative does not give a precipitate with bromine water.

These compounds resemble some of the natural tannins in many

ways, especially in their action towards bromine and towards iron salts.

When glyoxylic acid and paratoluidine act on one another, *paratoluidineacetoparatoluide*, $C_7H_7{\cdot}N{:}CH{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, is formed together with small quantities of paratoluidineacetic acid and *paratoluylparamethylimesatin*. The toluide is a pale red, amorphous powder, soluble in benzene and alcohol, insoluble in dilute alkalis. The imesatin crystallises in scales melting at 259° and soluble in alcohol, sparingly so in benzene. L. T. T.

Triacetylgallic acid. By Hugo Schiff (*Bull. Soc. Chim.*, 1894, [3], **11**, 770—771).—A question of priority with P. Sisley (this vol., i, 283) and A. Biétrix (Abstr., 1894, i, 130). Jn. W.

Syntheses by means of Ethylic Phenylmalonate. By Wilhelm Wislicenus and Karl Goldstein (*Ber.*, 1895, **28**, 815—818; compare Abstr., 1894, i, 376).—*Ethylic phenylmethylmalonate* may be prepared in the usual way, and boils at 165—166° (16 mm. pressure). It is usually accompanied by a little ethylic phenylacetate, probably formed by the action of water in the presence of sodium ethoxide. *Phenylmethylmalonic acid* melts and loses carbonic anhydride at 157°, hydratropic acid, CHMePh·COOH, being formed. *Ethylic phenylbenzylmalonate* boils at 224° (19 mm. pressure), and melts at 48—49°. The free *acid* melts and decomposes at 144°. Only a very small amount of the acid is formed when the ethylic salt is hydrolysed, the greater part being converted into benzylphenylacetic acid. A. H.

Some Mercury Compounds of the Aromatic Series. By August Michaelis (*Ber.*, 1895, **28**, 588—593).—Compounds HgR_2 (R = an aromatic residue) are obtained by heating the bromo-derivatives RBr in xylene solution at 180° with 1½—3 per cent. sodium amalgam in amount containing twice the theoretical quantity of sodium. By heating them with alcoholic mercuric chloride compounds, Cl·Hg·R are obtained, and the corresponding bromo- and iodo-compounds may be similarly prepared. By dissolving them in a hot solution of a fatty acid, HX, and diluting the solution with water, compounds X·Hg·R are obtained. The temperatures given below are melting points.

1 : 3-*Mercuryditolyl*, colourless to pale yellow needles, 102°. 1 : 3-*Mercurytolyl bromide*, white needles, 183—184°; *iodide*, white, nacreous plates, 161—162°; *formate*, needles, 106°; *acetate*, spherical aggregates of white needles, 83—84°; *propionate*, white needles, 102°. *Mercurydipseudocumyl*, white prisms, 189°. *Mercurypseudocumyl chloride*, needles, 201°; *bromide*, white powder, 211°; *iodide*, silky needles, 196—197°. *Mercurydimesityl*, silvery needles, 236°. *Mercurymesityl chloride*, needles, 200°; *bromide*, 194°; *iodide*, needles, 178°. *Mercurycymyl chloride*, 156°; *bromide*, 163°; *iodide*, 169°; all three crystallise in lustrous needles. *Mercurydiphenylenephenyl*, $Hg(C_6H_4Ph)_2$, lustrous scales, 216°; the halogen compounds form white powders, and melt above 325°. C. F. B.

Oxidation of Derivatives obtained by the Action of Ortho- and of Para-toluenesulphonic Chloride on Amido-compounds. By JULIUS TROEGER and PAUL W. UHLMANN (*J. pr. Chem.*, 1895, [2], **51**, 435—448).—The authors make the interesting observation that well-formed crystals of paratoluenesulphonic chloride emit a bright light when pressed with a metal spatula or when shaken in the vessel containing them; this phenomenon is only exhibited by freshly formed crystals.

The oxidation of para- and ortho-toluenesulphonic anilide with potassium permanganate in a solution periodically neutralised with sulphuric acid, produced para- and ortho-toluenesulphonamide respectively.

The *condensation product*, $C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, obtained from paratoluenesulphonic chloride and paramidophenol, crystallises in white needles, and melts at 143°; when oxidised by potassium permanganate in alkaline solution, it yields parasulphaminebenzoic acid, but if the oxidation occurs in neutral solution, paratoluenesulphonamide is produced. The *condensation product* of paratoluenesulphonic chloride with orthamidophenol crystallises in white needles, and melts at 138—139°, whilst that with metamidophenol melts at 157°; both yield paratoluenesulphonamide when oxidised in neutral solution.

The *condensation product* from paratoluenesulphonic chloride and phenylhydrazine, $C_6H_4Me{\cdot}SO_2{\cdot}N_2H_2Ph$, melts at 150—151°; its oxidation has not been thoroughly investigated. A. G. B.

Isomerism of the Diazosulphanilic acids and Diazo-ethers. By ARTHUR HANTZSCH (*Ber.*, 1895, **28**, 741—744).—Bamberger's observations on the transformation of paradiazosulphanilic acid into its isomeride by the action of soda (Abstr., 1894, i, 295) cannot be confirmed. The acid condenses only in presence of alkali, whilst the iso-anti-salt does not form dyes even after remaining for weeks. Diazobenzenesulphonic acid behaves in a similar manner, and is little changed by 4 per cent. soda at ordinary temperatures even after several days' treatment. Iso-anti-nitrodiazobenzene cyanide combines directly with β-naphthol, but more slowly than the syn-derivative, and as the solution contains OH, not H, ions, isomeric change could not occur. The power of direct condensation shown by nitrodiazobenzene ether is therefore no proof that it does not belong to the iso-series (compare Bamberger, this vol., i, 134, and v. Pechmann, this vol., i, 215). In answer to Bamberger's other criticisms (this vol., i, 134 and 215), it is pointed out that the formation of normal potassium diazobenzene from various diazo-ethers is inconclusive, since the same compound is formed by the hydrolysis of nitrosoacetanilide. As Bamberger obtained ethers readily from the iso-anti-silver compounds, but not from the normal salts, the ethers should, according to his theory, belong to the same series. His results therefore confirm the author's view that the normal syn-ethers are incapable of existence. J. B. T.

Hydrolysis of the Ethereal Salts of Sulphonic acids by Alcohols. By J. H. KASTLE and PAUL MURRILL (*Amer. Chem. J.*, 1895, **17**, 290—297).—Krafft and Roos (Abstr., 1892, 1219; 1894, i, 91) have shown that the ethereal salts of sulphonic acids—in contradistinction to those of carboxylic acids—readily undergo hydrolysis when treated with alcohol, and can therefore be used for the preparation of ethers (alkyl oxides). The authors have studied the hydrolysis of ethylic benzenesulphonate, and ethylic parachlor-, parabrom-, and pariodo-benzenesulphonates in the presence of various alcohols. The last-named salt, $C_6H_4I\cdot SO_3Et$, is new, and was prepared by treating the corresponding sulphochloride with sodium ethoxide. It separates from ether in large, four-sided, transparent prisms, and melts at 51°.

Tables and curves showing how the amount of ethereal salt hydrolysed varies (1) with the amount of alcohol present, (2) with the kind of alcohol used, and (3) with the temperature, are given. The general conclusions arrived at are as follows:—(1) The ethereal salts of sulphonic acids are readily hydrolysed by alcohols. (2) The rate of hydrolysis increases with the temperature. (3) Of the alcohols tried (methylic, ethylic, normal- and iso-propylic alcohol); methylic alcohol is the most effective, the others seem to have practically the same effect. (4) The ethereal salts of halogen sulphonic acids are more readily hydrolysed than the corresponding salts of simple sulphonic acids; and the rate of hydrolysis appears to be independent of the nature of the halogen atom, as the ethereal salts of parachlor-, parabrom-, and pariodo-benzenesulphonic acids practically are hydrolysed to the same extent when treated with alcohol for a given time. J. J. S.

Action of Alkali Sulphites on Aromatic Diazo-compounds. By HANS V. PECHMANN (*Ber.*, 1895, **28**, 863—868).—Spiegel (Abstr., 1885, 987) has shown that compounds containing the azo-group are capable of uniting with alkali hydrogen sulphites to form additive compounds; it is now shown that compounds which contain the diazo-group have the same property. Thus potassium sulphanilic-diazosulphonate, $SO_3K\cdot C_6H_4\cdot N{:}N\cdot SO_3K$, when treated with potassium sulphite, gives the salt of a trisulphonic acid,

$$SO_3K\cdot C_6H_4\cdot N(SO_3K)\cdot NH\cdot SO_3K.$$

This salt is very soluble in water, but can be precipitated with alcohol. It crystallises with $3H_2O$, and on heating with hydrochloric acid is hydrolysed into sulphuric acid and phenylhydrazineparasulphonic acid. This salt is characterised by its remarkable stability in the presence of Fehling's solution. When diazobenzene potassium sulphonate is heated for some time with a solution of potassium hydrogen sulphite, the main product is not a simple additive compound, but a salt of sulphanilic-hydrazo-sulphonic acid,

$$SO_3K\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3K.$$

The formation of this salt is due to the removal of a sulphonic acid group from the side chain into the benzene nucleus, a phenomenon

similar to that observed by A. W. Hofmann and Martius in the case of the substituted aromatic amines.

The author thinks it probable that the first product formed on sulphonating an aromatic base is one in which the sulphonic group is in the side chain, and that this sulphonic group then replaces an atom of hydrogen in the benzene nucleus. J. J. S.

Benzenesulphinic acid Derivatives of Diazobenzene. By HANS V. PECHMANN (*Ber.*, 1895, **28**, 861—863).—The author considers that if the two isomeric series of benzenediazosulphonates described by Hantzsch (Abstr., 1894, i, 455) are really stereoisomerides as Hantzsch asserts, then the probability is that the benzenediazosulphinic acids will also exist in two isomeric forms; but if the diazosulphonates are structurally isomeric, the isomerism depending on the tautomeric nature of the sulphonic acid group, as Bamberger (this vol., i, 25), E. Fischer (Abstr., 1894, i, 597), and A. Claus (Abstr., 1894, i, 597) believe, then the diazosulphinic acids will exist in one form only. From a study of the action of benzenesulphinic acid on diazobenzene and on paranitrodiazobenzene, under varying conditions, the author is led to the view that diazobenzene benzenesulphinate, $Ph{\cdot}N_2{\cdot}SO_2Ph$, and benzenesulphoparanitrodiazobenzene, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_2Ph$, each exist in only one modification. The stereochemical theory of Hantzsch thus receives no support from the study of the sulphinic acids. J. J. S.

A New Mode of Preparing Derivatives of Indole. By EMIL FISCHER and HUGO HÜTZ (*Ber.*, 1895, **28**, 585—587).—When α-benzoïnoxime, $NOH{:}CPh{\cdot}CH(OH){\cdot}C_6H_5$, is dissolved in strong sulphuric acid, and the solution allowed to remain, it is converted almost quantitatively into *2′-phenylindoxyl*, $CPh\lessgtr^{C(OH)}_{NH}>C_6H_4$; zinc chloride at 100° effects the same transformation, but the yield is not so good. Neither β-benzoïnoxime nor deoxybenzoïnoxime (α) nor phenylacetoxime (? phenylacetaldoxime) undergo a simliar transformation.

2′-Phenylindoxyl crystallises in small, lustrous, yellow needles, and melts at about 175° when quickly heated. It is reduced to 2′-phenylindole by zinc and acetic acid, or by hydriodic acid in acetic acid solution. C. F. B.

Derivatives of Phenylindoxazen. By PAUL COHN (*Monatsh.*, 1894, **15**, 645—664).—When phenylindoxazen (10 grams) is warmed for half an hour with 40 per cent. anhydrosulphuric acid (60 c.c.), *phenylindoxazendisulphonic acid* is formed, which yields the following derivatives:—A *barium salt*, $C_{13}H_7NO_7S_2Ba + H_2O$, which crystallises from hot water in white scales; a *lead salt*, $C_{13}H_7NO_7S_2Pb$, which is anhydrous; a *sodium salt*, $C_{13}H_7NO(SO_3Na)_2 + 2H_2O$, which, on fusion with potash, yields a product melting at 189°, and containing 60·6 per cent. of carbon and 3·71 per cent. of hydrogen; a *potassium salt*, $C_{13}H_7NO(SO_3K)_2 + H_2O$; a *silver salt*, $C_{13}H_7NO_7Ag_2$; and a *sulphonamide*, which melts at 187—188°.

On bromination, phenylindoxazen yields a *dibromo-derivative*,

$C_{13}H_7NOBr_2$, which crystallises in small, white needles, melts at 148—149°, and does not lose bromine when boiled in a reflux apparatus with sodium ethoxide for 4 hours.

On reduction of its alcoholic solution with sodium, phenylindoxazen is converted into *phenylorthocresolamine*, $HO{\cdot}C_6H_4{\cdot}CHPh{\cdot}NH_2$, which melts at 102—103°, has a slight aromatic odour, dissolves readily in acids and alkalis, and yields the following salts (R = $C_{13}H_{13}NO$):—*hydrochloride*, RHCl, which melts at 194—196°; *platinochloride*, $R_2H_2PtCl_6$, which crystallises in orange-yellow needles; *hydriodide*, RHI, which crystallises in silky white needles softening at 180°; *sulphate*, $R_2H_2SO_4$, which softens at 180°, and *nitrate*, $RHNO_3 + H_2O$, which melts at 98°. The *oxalate*, *picrate*, *tartrate*, and *dibenzoate* are also described. The last-named, $C_{27}H_{21}NO_3$, melts at 176°, and on boiling with alcoholic soda gives the *monobenzoyl derivative*, $C_{20}H_{17}NO_2$, which melts at 208°. G. T. M.

2 : 2′-Hydroxydiphenylcarboxylic Lactone (Diphenylmethylolid). By CARL GRAEBE and P. SCHESTAKOW (*Annalen*, 1895, **284**, 306—324).—Diphenylmethylolid and xanthone are related in a similar manner to phenanthraquinone and anthraquinone respectively; the steps by which the former substance is obtained from phenanthraquinone include the preparation of the amide of fluorenonecarboxylic acid (Wegerhoff, Abstr., 1888, 1201), orthamidofluorenone, and orthohydroxyfluorenone, the latter, on treatment with fused potash, giving rise to 2 : 2′-hydroxydiphenylcarboxylic acid, which is at once converted into the lactone.

Orthamidofluorenone, $\begin{matrix}NH_2{\cdot}C_6H_3\\ \vert \\ C_6H_4\end{matrix}\!\!>\!O$, is obtained by the action of potassium hypobromite on the amide of fluorenonecarboxylic acid. It crystallises in long, slender, reddish-yellow needles, and melts at 138°; it distils without undergoing decomposition. Fusion with caustic potash converts it into phenanthridone. The *hydrochloride* and *sulphate* are decomposed by water and alcohol; nitrous acid gives rise to a *diazo*-derivative, which yields hydroxyfluorenone on treatment with boiling water. During the preparation of orthamidofluorenone in the manner described, a varying amount of the *nitrile* of orthofluorenonecarboxylic acid is produced; it crystallises from alcohol in yellow needles, and melts at 244°.

Orthohydroxyfluorenone, $\begin{matrix}HO{\cdot}C_6H_3\\ \vert \\ C_6H_4\end{matrix}\!\!>\!O$, is prepared by adding sodium nitrite to the ice-cold solution of orthamidofluorenone in concentrated hydrochloric acid; it forms orange-red crystals, and melts at 249° (corr.), subliming and distilling without decomposition. It is readily soluble in alkalis, and, when warmed, in alkali carbonates. Treatment with fused potash converts it into a mixture of 2 : 2′- and 2 : 6-hydroxydiphenylcarboxylic acids.

2 : 2′-*Dihydroxydiphenylcarboxylic lactone*, $\begin{matrix}C_6H_4{\cdot}CO\\ \vert \quad \vert \\ C_6H_4{\cdot}O\end{matrix}$, is obtained by the action of fused potash on orthohydroxyfluorenone, 2 : 2′-hydroxydiphenylcarboxylic acid being the intermediate product; it is identical

with Richter's hydroxydiphenyleneketone (Abstr., 1884, 324), prepared by the action of phosphorus oxychloride on sodium or methylic salicylate, and subsequently by Griess by heating phenol with the sulphate of orthodiazobenzoic acid on the water bath (Abstr., 1888, 588), this method of preparation also giving rise to phenylsalicylic acid and 2 : 4′-hydroxydiphenylcarboxylic acid. It crystallises from alcohol in needles, and melts at 92·5° (corr.); on adding silver nitrate to the neutral solution of the potassium salt, silver hydroxydiphenylcarboxylate is formed. It is readily soluble in alkalis, whilst alkali carbonates dissolve it only when warmed, and a current of carbonic anhydride reprecipitates the lactone. It is indifferent towards phenylhydrazine and reducing agents, and when distilled with zinc dust yields diphenyl; distillation from lime gives rise to diphenylene oxide and benzophenone, whilst the calcium salt of 2 : 2′-hydroxydiphenylcarboxylic acid gives rise to 2-hydroxydiphenyl when submitted to dry distillation.

2 : 6-*Hydroxydiphenylcarboxylic acid* is one of the products of the action of fused potash on orthohydroxyfluorenone. It crystallises from water with $1H_2O$, which is lost at 100°; the anhydrous salt melts at 154° (corr.). Treated with excess of lime water, it forms a *dicalcium* salt, which becomes converted into the *monocalcium* salt under the influence of carbonic anhydride. The lactone is not formed on treating the acid with acetic chloride, and the action of cold, concentrated, sulphuric acid converts it into orthohydroxyfluorenone. The *methylic* salt melts at 84—85°, and distils without undergoing decomposition; the *ethylic* salt crystallises from alcohol in plates, and melts at 111°. The amide is obtained by heating the ammonium salt in sealed tubes for six hours at 250—260°; it crystallises from alcohol in needles, and melts at 262—263°.

4′ : 2-*Hydroxydiphenylcarboxylic acid* is formed during the preparation of diphenylmethylolid from phenol and orthodiazobenzoic acid; it melts at 206·5°, and its properties agree with those of the substance described by Griess (*loc. cit.*). M. O. F.

Action of Ethylic Oxalate on Dibenzyl Ketone. By Ludwig Claisen and Thomas Ewan (*Annalen*, 1895, **284**, 245—299; compare Abstr., 1888, 676, and 1891, 425).—Continuing the investigation of the behaviour of ethylic oxalate towards ketones (*loc. cit.*), the authors have included diethyl ketone and dibenzyl ketone in their experiments.

Diethyl ketone, when mixed with ethylic oxalate (1 mol.) and treated with ice-cold alcoholic sodium ethoxide (1 mol.), gives rise to a *compound*, $C_7H_8O_3$, with elimination of 2 mols. of ethylic alcohol. The same substance is produced when methylic oxalate and sodium methoxide are employed; it melts at 142—143°, and has strongly acid properties. An intense, dark-green coloration is developed in the alcoholic solution by ferric chloride.

Oxalyldibenzyl ketone, $C_{17}H_{12}O_3$, is obtained by adding a mixture of dibenzyl ketone (1 mol.) and ethylic oxalate (1 mol.) to an ice-cold solution of sodium (2 mols.) in absolute alcohol; the liquid, which at first becomes brown and finally bluish-violet, is cooled for a few

hours, and then allowed to remain at the ordinary temperature for two days. The same compound is produced when methylic oxalate and methylic alcohol are used. It crystallises in short, sulphur-yellow prisms, and melts at 192—193°; at 194—196° it resolidifies, and melts finally at 240°. The alcoholic solution gives a yellowish-brown or brownish-green coloration with ferric chloride, according to the quantity of reagent employed, whilst copper acetate also colours the liquid yellowish-brown; if the solution is dilute, the latter reagent produces a yellowish coloration, which becomes green, a yellow copper salt being precipitated. When heated with oxalyldibenzyl ketone dissolved in sodium carbonate, Fehling's solution is at once reduced; on adding fuming nitric acid to the solution in glacial acetic acid, and pouring the liquid into water, a yellow precipitate is formed, which dissolves in alkalis with a blue colour. Oxalyldibenzyl ketone has strongly acid properties, and is not completely precipitated from solutions of its salts by acetic acid, whilst an aqueous solution of potassium acetate dissolves it when heated on the water bath; the *sodium* and *potassium* salts are yellow, and the *silver* salt is not decomposed by light. On adding one drop of caustic soda to a solution of the sodium salt, a yellow coloration is produced, becoming brownish-violet, whilst the liquid acquires an intense, bluish-violet colour on further addition of alkali. When oxalyldibenzyl ketone is heated with aqueous potash for half an hour, it is decomposed into dibenzyl ketone and oxalic acid. Ammonia converts it into a *compound*, $C_{17}H_{11}O_2{\cdot}NH_2$, which separates from glacial acetic acid in compact, lustrous crystals, and melts at 151—152°; it dissolves in alkalis and alkali carbonates, gives a brownish-green coloration with ferric chloride, and yields an *isomeride* when heated at 200°. This substance crystallises in lustrous, yellow leaflets, and melts at 226—227°; the solution in sodium carbonate is yellow, and does not yield ammonia when boiled, differing in this respect from the first modification. The *anilide*, $C_{17}H_{11}O_2{\cdot}NHPh$, crystallises from alcohol in short, yellow needles, and melts at 175—176°; it is insoluble in aqueous alkalis, which dissolve it, however, if alcohol is previously added, the first few drops producing a violet coloration. Acetic acid precipitates the anilide and the two isomeric ammonium derivatives from the solutions in alkali. Orthotolylenediamine gives rise to a *compound*, $C_{24}H_{18}N_2O$, which crystallises in orange-coloured plates, and melts at 290—291°; the alcoholic solution exhibits fluorescence, yellow in transmitted, green by reflected light. The *phenylhydrazone*, $C_{17}H_{12}O_2{:}N{\cdot}NHPh$, melts at 181—182°, and the solution in concentrated sulphuric acid is deep red, becoming blue on the addition of ferric chloride; it has acid properties, and is precipitated from the solutions in alkalis by acetic acid. Hydroxylamine gives rise to a *derivative*, $C_{17}H_{13}NO_3$, which in behaviour more closely resembles a carboxylic acid than an oxime; it melts and decomposes at 183—184°, and is precipitated from alkaline solutions on the addition of mineral acids only.

The *acetyl* derivative of oxalyldibenzyl ketone crystallises in yellow needles, and melts at 103—104°; it has acid properties, and the *potassium* salt, which is deep violet, yields oxalyldibenzyl ketone when the aqueous solution is treated with hydrochloric acid.

The *methylic* salt, $C_{17}H_{11}O_3Me$, is obtained by acting on the dry silver salt of oxalyldibenzyl ketone with methylic iodide; it crystallises in short, yellow needles, and melts at 94—95°. Although scarcely soluble in cold, aqueous potassium carbonate, it dissolves readily when heated, with production of an intense, violet coloration. It is hydrolysed by hot aqueous alkalis.

The isomeric *methyl* derivative, $C_{17}H_{11}O_3Me$, is obtained by adding methylic iodide to an alcoholic solution of the disodium salt of oxalyldibenzyl ketone; it crystallises in sulphur-yellow leaflets, and melts at 167°. It dissolves in aqueous potassium carbonate, and on adding silver nitrate to the neutral solution the *silver* salt is precipitated. The action of hot aqueous alkali gives rise to oxalic acid and *methyldibenzyl ketone*, $CHPhMe{\cdot}CO{\cdot}CH_2Ph$, an oil which boils at 320—326°, and yields a *phenylhydrazone*, which melts at 92—93°. The *acetyl* derivative, $C_{17}H_{10}O_3MeAc$, crystallises in short, yellow prisms, melts at 111—112°, and dissolves in alkali carbonates.

The *dimethyl* derivative, $C_{17}H_{10}O_3Me_2$, is obtained by the action of methylic iodide on the silver salt of the foregoing compound. It crystallises in lustrous, yellow cubes, and melts at 79°. Although insoluble in cold alkalis and alkali carbonates, it yields the monomethyl derivative when boiled for several hours with aqueous potash.

Oxalyldibenzyl ketone is oxidised by potassium permanganate, with formation of benzoic and oxalic acids, and a *compound*, $C_{17}H_{10}O_3$ or $C_{34}H_{22}O_6$. The latter, however, is more conveniently obtained by the action of mercuric oxide suspended in the hot, aqueous solution; it crystallises from ethylenic bromide in pale yellow plates, becomes brown at 225°, and melts at 237—239°, undergoing decomposition; the substance retains the solvent from which it is crystallised. Ferric chloride develops in the alcoholic solution a dark, brownish-green coloration, whilst copper acetate gives rise to a yellow precipitate; Fehling's solution is not reduced when boiled with the substance. It dissolves in alkalis, alkali carbonates, and, on heating, in alkali acetates, and the dilute alcoholic solution is strongly acid. The *sodium* salt contains $3H_2O$; the *silver* salt is yellow.

When heated at 225—230°, oxalyldibenzyl ketone is converted into an isomeride, which crystallises in silvery, greyish-yellow leaflets, and melts at 248—249°, undergoing decomposition. *Iso-oxalyldibenzyl ketone* has strongly acid properties; the *potassium* and *sodium* salts contain $4H_2O$, and the solution of the latter does not become violet on adding excess of alkali. The *barium* salt contains $8H_2O$; the *silver* salt is not readily decomposed by light, and the *methylic* salt appears to be an oil. The *acetyl* derivative crystallises from methylic alcohol in pale yellow needles, and melts at 137—139°.

When oxidised with potassium permanganate, iso-oxalyldibenzyl ketone gives rise to benzaldehyde, and oxalic, benzoic, and benzoylformic acids. On reduction with sodium amalgam, a *dihydro*-derivative, $C_{17}H_{14}O_3$, is produced; it crystallises from glacial acetic acid in colourless leaflets, and melts at 220—221°.

The behaviour of iso-oxalyldibenzyl ketone towards hot aqueous alkalis has an important bearing on the question of its constitution. Whilst potash decomposes it into dibenzylglycollic acid (m. p.

157—158°) and carbonic anhydride, treatment with aqueous barium hydroxide gives rise to dibenzyl ketone, phenylacetic, phenylpyruvic, and dibenzylglycollic acids, together with a dibasic *acid* of the formula $C_{17}H_{16}O_5$. A close comparison of the chemical characteristics of iso-oxalyldibenzyl ketone and dibenzyloxalylcarboxylic acid lactone (Volhard, this vol., i, 100), supplemented by an examination of their toxic properties, renders it probable that these two substances differ only tautomerically. In order to emphasise the relation of iso-oxalyldibenzyl ketone to derivatives of pulvic acid, the authors propose to term it *pulvinone*.

Consideration of the properties of oxalyldibenzyl ketone leads to the formula $CHPh<\begin{matrix}CO\cdot CPh\\ \|\\ CO\cdot C\cdot OH\end{matrix}$ as expressing its constitution, whilst the isomeric pulvinone is represented by the formula

$$CHPh{:}C<\begin{matrix}C(OH){:}CPh\\ |\\ O\text{——}CO\end{matrix}.$$

M. O. F.

Phenolphthaleïn Derivatives. By Albin Haller and Alfred Guyot (*Compt. rend.*, 1895, **120**, 296—299).—The action of phthalic chloride on phenylic ethylic ether in presence of aluminium chloride yields the *diethylphenolphthaleïn*, $\begin{matrix}C_6H_4\\ |\\ CO\cdot O\end{matrix}>C(C_6H_4\cdot OEt)_2$, a white, crystalline compound, very soluble in benzene, much less soluble in alcohol or ether. It dissolves in concentrated sulphuric acid, forming a red solution, from which it is precipitated without alteration, on dilution.

When boiled with ethylic iodide in presence of sodium ethoxide, phenolphthaleïn yields a diethyl derivative identical with the preceding compound, and not a diethyl derivative with a quinonoïd constitution. If either of the products is heated with alcoholic potash, it yields slender, white needles of the salt,

$$COOK\cdot C_6H_4\cdot C(C_6H_4\cdot OEt)_2\cdot OH,$$

which gradually dissociates in presence of water, regenerating diethylphenolphthaleïn, thus resembling the dibenzyl derivative. Sodium amalgam or zinc powder in presence of aqueous potash readily and quantitatively converts the diethyl derivative, by whichever method prepared, into *diethoxytriphenylmethaneorthocarboxylic acid*, $COOH\cdot C_6H_4\cdot CH(C_6H_4\cdot OEt)_2$; this forms colourless crystals melting at 135°, and somewhat soluble in the ordinary solvents, and in solutions of alkali hydroxides and carbonates; sulphuric acid in the cold converts it into a well-crystallised phthalidin.

Although there is no evidence of a quinonoïd grouping in diethylphenolphthaleïn, the author does not consider that it necessarily follows that phenolphthaleïn has not a quinonoïd function in alkaline solution.

C. H. B.

Formation of Diphthalyl. By Guido Goldschmiedt (*Monatsh.*, 1895, **16**, 13—16).—When phthalide and ethylic-ψ-opianate are heated together in molecular proportion at 280—290°, diphthalyl, in yield of

from 4 to 5 per cent., is obtained. When dissolved in concentrated sulphuric acid, it forms a pale yellow solution having a strong blue fluorescence, and on the addition of sulphuric acid containing a trace of nitric acid to this solution, an evanescent emerald-green coloration is observed. These colour reactions afford a convenient method of characterising diphthalyl (compare Gräbe and Guye, Abstr., 1886, 882).

G. T. M.

Hexamethyltriamidotriphenylmethane Derivatives. By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1895, **120**, 192—194, 264—266, and 331—333).—When sodium hydroxide is added to a boiling solution of hexamethyltriamidotriphenylmethane chloride in methylic, ethylic, or amylic alcohol, the product is not the carbinol corresponding with the chloride, but an ether of the type $OR{\cdot}C(C_6H_4{\cdot}NMe_2)_3$. When R = Me or Et the product is crystalline, but the amylic derivative is viscous. When treated with methylic iodide in the cold in presence of water or alcohol, these derivatives, as well as the corresponding carbinol and hydride, all combine with three molecules of methylic iodide, yielding crystalline, white or sulphur-yellow products, soluble in water and in alcohol, but insoluble in other organic solvents. They decompose below 100° with loss of methylic iodide, and become blue. When heated with alcoholic soda, the original triamine is obtained together with the intermediate products described below. Silver oxide removes the iodine and forms powerful bases which combine with hydrogen iodide and behave like the octomethylleucaniline of Hofmann and Girard. The solubilities of the five compounds at 16—20° show considerable differences; the carbinol is more soluble than the hydride, and the solubility of the ethereal salts increases with the molecular weight of the introduced alkyl radicle.

The action of methylic iodide on hexamethyltriamidotriphenylmethane gives rise to intermediate products which become green in contact with hot acetic acid, but only one of these could be isolated. The methoxide, $OMe{\cdot}C(C_6H_4{\cdot}NMe_2)_3$, is mixed with water and methylic iodide, and allowed to remain at the ordinary temperature for several days, until, in contact with dilute acetic acid, a green colour is produced instead of a violet. The product is then mixed with water, the excess of methylic iodide removed by distillation, and the liquid filtered. The triiodo-compound is in the solution; the intermediate product remains on the filter and is purified by crystallisation from methylic alcohol. The *moniodotrimethylammoniumtetramethyldiamidotriphenylmethane methoxide*, $OMe{\cdot}C(C_6H_4{\cdot}NMe_2)_2{\cdot}C_6H_4{\cdot}NMe_3I$, thus obtained is white and crystalline; when dissolved in dilute acetic acid and mixed with a small quantity of an aqueous solution of potassium iodide, it yields a lustrous crystalline mass of the compound

$$CI(C_6H_4{\cdot}NMe_2)_2{\cdot}C_6H_4{\cdot}NMe_3I + H_2O,$$

which is the lower homologue of "iodine-green" and like the latter is unstable. When heated, it loses water and methylic iodide, and yields hexamethyltriamidotriphenylmethane iodide, but if heated in a current of methylic iodide vapour at 100° it loses water only.

The moniodo-ammoniums corresponding with the other four triamines are formed when the triiodoammoniums are treated with aqueous

soda in the case of the ethylic and amylic compounds, or alcoholic soda in the case of the lower terms; after boiling for some hours and then adding acetic acid a green product is obtained. In the case of the derivative of the hydride, lead peroxide must be added with the acetic acid, and the iodide $Cl(C_6H_4\cdot NMe_2)_2\cdot C_6H_4\cdot NMe_3I$ is formed.

The compounds described above include three that are coloured and eleven that are colourless, but six of the latter can be converted into coloured compounds by double decomposition. They are as follows—

Coloured compounds.—$CCl(C_6H_4\cdot NMe_2)_3$, and the corresponding iodide, and $Cl(C_6H_4\cdot NMe_2)_2\cdot C_6H_4\cdot NMe_3I$.

Colourless compounds yielding coloured products.—$CH(C_6H_4\cdot NMe_2)_3$, $OH\cdot C(C_6H_4\cdot NMe_2)_3$, and the corresponding methylic, ethylic, and amylic ethers, and $OMe\cdot C(C_6H_4\cdot NMe_2)_2\cdot C_6H_4\cdot NMe_3I$.

Colourless compounds yielding colourless products.—$CH(C_6H_4NMe_3I)_3$, $OH\cdot C(C_6H_4\cdot NMe_3I)_3$, and the corresponding methylic, ethylic, and amylic ethers.

The coloured compounds have a negative element or an acid radicle united with the carbon of the methane nucleus, the three other valencies of this carbon being satisfied by the amidophenyl group in which the nitrogen is trivalent, except in the third compound where one of the nitrogens is quinquevalent. This characteristic is shared by the compounds in the second group, but in these the radicle saturating the fourth valency of the methane carbon shows considerable chemical activity, and when positive can be displaced by a negative radicle and *vice versâ*, a negative radicle producing a coloured compound and a positive radicle a colourless one.

In the third group of compounds, the nitrogen of the amidophenyl groups is in all cases quinquevalent, and the univalent groups H, OH, OMe, &c., are no longer replaceable by negative radicles. The complete saturation of the nitrogen therefore involves the immobility of the positive radicle attached to the methane carbon, and this gives the whole molecule a much higher stability.

In the carbinol $OH\cdot C(C_6H_4\cdot NMe_3I)_3$ the hydroxyl group cannot be displaced by an acid radicle, but can be displaced by an alkyl group, and in this respect it resembles triphenylcarbinol, the saturation of the nitrogen imparting to the group $C_6H_4\cdot NMe_3I$ functions similar to those of the group C_6H_5.

The alcoholic function of triphenylcarbinol resembles that of acids, and the corresponding chloride is decomposed by cold water; the alcoholic function of $OH\cdot C(C_6H_4NMe_2)_3$, on the other hand, is of the same order as that of metallic hydroxides, since it reacts with acids, and the amidocarbinols in general displace ammonia from its salts. The intermediate condition is represented by the diamidocarbinols.

C. H. B.

Triphenylmethane Colouring Matters. By Albin Haller and Paul Th. Muller (*Compt. rend.*, 1895, **120**, 410—413).—Ebullioscopic determinations lead to the conclusion that the chlorides of the colouring matters of the amidotriphenylmethane group are not dissociated in water, whereas ammonium chloride, aniline hydrochloride, and nitrosodimethylaniline hydrochloride show considerable dissociation.

This result supports Rosenstiehl's view as to the constitution of the rosaniline and other triphenylmethane colouring matters.

C. H. B.

Preparation of α-Naphtholcarbothionylic acid. By RICHARD PŘIBRAM and CARL GLÜCKSMANN (*Monatsh.*, 1894, **15**, 605—612; compare Abstr., 1893, i, 75).—On heating α-naphthol (20 grams) with potassium thiocarbonate (30 grams) in sealed tubes at 125—130°, *α-naphtholcarbothionylic acid* is obtained in yield of about 10 per cent. It is a dark yellow powder, which gives a red coloration with alkaline solutions, is only sparingly soluble in alcohol, ether, water and benzene, and melts with decomposition at 110°. A better yield (70 per cent.) of the acid is obtained on heating together α-naphthol, potassium xanthate, and alcohol, at 100°. The potassium derivative of α-naphthol and carbon bisulphide, when heated in sealed tubes at 100°, also combine with formation of the potassium salt of α-naphtholcarbothionylic acid.

G. T. M.

Synthesis of Anthracene. By MAURICE DELACRE (*Compt. rend.*, 1895, **120**, 155—157).—The action of ethylic trichloracetate on benzene in presence of aluminium chloride yields a product which crystallises readily in bulky needles, melting at 219°. When more strongly heated, it yields carbonic anhydride and a hydrocarbon which melts at 115° and boils at about 300°. The exact nature of the first product and of the hydrocarbon derived from it were not ascertained.

The action of phenylic trichloracetate on benzene in presence of aluminium chloride, yields an ethereal salt which is difficult to isolate but which when distilled splits up into carbonic anhydride and anthracene, about 9 grams of the latter being obtained from 20 grams of phenylic trichloracetate.

C. H. B.

Orientation in the Terpene Series. By ADOLF BAEYER (*Ber.*, 1895, **28**, 639—652, and 652—654; compare Abstr., 1894, i, 535, and this vol., i, 152).—*d*-Carone, obtained from caraway oil, has $[\alpha]_D = +173{\cdot}8°$; the sp. gr. is 0·9567. *l-Carone*, derived from balm-mint (*Mentha crispa*) oil, has $[\alpha]_D = -169{\cdot}5°$. Each modification forms a liquid oxime, and on mixing the two, the oxime of *i*-carone separates; it crystallises in long prisms, and melts at 77—79°. The *semicarbazide compound* of the inactive modification melts at 178°.

d-*Bisnitrosocarone*, $(C_{10}H_{15}O)_2N_2O_2$, is obtained by cautiously adding acetic chloride to a well-cooled mixture of *d*-carone and amylic nitrite; it crystallises in small, colourless plates, and decomposes and evolves gas at 112—118°, a green coloration being developed. This substance closely resembles bisnitrosylbenzyl (Behrend and Königs, Abstr., 1890, 1122), differing from it, however, in its behaviour on treatment with hydrolysing agents; this is probably due to its tertiary character, whilst bisnitrosylbenzyl must be regarded as a primary bisnitroso-derivative. i-*Bisnitrosocarone* crystallises in rhombic plates; it melts and decomposes at 145°.

Caronedinitrosylic acid, $C_{10}H_{15}O\cdot N_2O_2\cdot H$, is formed when bisnitrosocarone is treated with an ice-cold solution of hydrogen chloride in absolute alcohol. It melts and decomposes at 80—90°, and in many respects resembles nitroso-β-benzylhydroxylamine, obtained by the action of nitrous acid on β-benzylhydroxylamine (Behrend and Königs, Abstr., 1891, 1034).

The *dinitrin*, $C_{20}H_{32}N_2O_2$, obtained by reducing dinitrosocarone in alcoholic solution with sodium amalgam, melts at 120—130°; it undergoes decomposition spontaneously at ordinary temperatures, and also on treatment with cold mineral acids, in which it is very readily soluble. On reducing bisnitrosocarone with sodium amalgam, a certain quantity of *d*-carone is regenerated. The *dinitrosone*, $C_{20}H_{32}N_2O_4$, is formed on adding sodium hypochlorite to a solution of caronedinitrosylic acid in sodium carbonate.

Nitrosomenthone, nitrosodihydroeucarvone, and *nitrosocarveol*, which melts and decomposes at 133°, are bisnitroso-derivatives. Nitrosopinene, on the other hand, is an isonitroso-derivative, forming sodium and methylic salts, and yielding carvacrol when boiled with dilute hydrochloric acid for half an hour. In order to distinguish between carvacrol and thymol, a very dilute, alkaline solution of the phenol is treated with sodium nitrite and acidified; after some hours yellow needles are deposited, and on adding acetic acid to the solution of these crystals in ammonia, a solid, amorphous precipitate of the nitroso-derivative is formed if thymol is present, whilst carvacrol gives rise to oily drops which soon become crystalline. The formation of carvacrol when nitrosopinene is treated with boiling hydrochloric acid is not in accordance with Bredt's expression for the constitution of pinene, which demands the production of thymol under these conditions.

It is found that pinene and limonene nitrosochlorides are bisnitroso-derivatives belonging to the class of secondary compounds.

The *semicarbazide compound* of pulegone crystallises from alcohol and melts at 172°; on treating it with boiling dilute acids, pulegone is regenerated.

Pulegone hydrochloride is obtained on adding pulegone to a cooled solution of hydrogen chloride in glacial acetic acid, the liquid being afterwards poured on to ice; it melts at 24—25° (compare Beckmann and Pleissner, Abstr., 1891, 936). The hydrochloride yields pulegone when treated with a solution of potash in methylic alcohol; it is more stable than the hydrobromide, from which pulegone is regenerated on treatment with silver acetate and acetic acid.

Nitrosopulegone, $C_{10}H_{18}O\cdot NO$, is obtained in long, slender needles; ammonia dissolves it, giving rise to an oxime. Nitrosopulegone is probably a secondary bisnitroso-derivative. M. O. F.

Fenchone. By Otto Wallach (*Annalen*, 1895, **284**, 324—345; compare Abstr., 1893, i, 105 and 596).—A direct comparison has been made of metacymene obtained by the action of phosphoric anhydride on fenchone (*loc. cit.*) with metacymene isolated by Kelbe from resin oil, and it is found that the hydrocarbons are identical.

Tetrahydrofenchene, $C_{10}H_{20}$, is formed when fenchylic alcohol is

heated with phosphorus and hydriodic acid for 15 hours at 210—215°; it is a colourless oil which boils at 160—165°. The sp. gr. = 0·7945 at 22°, and the refractive power is $[n]_D = 1·4370$. The hydrocarbon is also obtained by reducing fenchone and fenchylamine under the conditions described; it is not identical, however, with the hydrocarbon formed on reducing fencholenic acid (Abstr., 1892, 1237), but in physical properties it closely resembles the tetrahydropinene obtained from pinene hydrochloride (Abstr., 1892, 998), although the two compounds are not identical. It resists the action of potassium permanganate and of fuming nitric acid in the cold; the *bromide* crystallises from ethylic acetate and melts at 200°.

Fenchocarboxylic acid, $C_{11}H_{16}O_3$ or $C_{11}H_{18}O_3$, is formed on passing a current of carbonic anhydride through a solution of fenchone in ether to which sodium has been added; it has not been obtained free from acetic acid and fenchylic alcohol, and in this condition melts at 77—78°. The *lead* salt is amorphous. When submitted to dry distillation, the acid decomposes into carbonic anhydride and an unsaturated *acid*, $C_{11}H_{16}O_2$, which crystallises from alcohol in lustrous leaflets, and from ether in prisms, melting at 173—174°. It sublimes without undergoing change, is volatile in an atmosphere of steam, and is lævorotatory. The *silver* salt is unstable, and dissolves in alcohol and ether.

During the preparation of fenchocarboxylic acid, fenchylic alcohol is obtained in considerable quantity; it melts at 45° (compare Abstr., 1891, 1086). When added to a solution of phosphorus and iodine in carbon bisulphide, it yields a fenchylic phosphite which crystallises in needles and melts above 300°; if chlorine is employed, fenchylic chloride is formed, together with an *isomeride* which melts at 195—196°, and has an odour of camphor. The acid of the formula $C_{10}H_{16}O_3$, obtained by oxidising fenchone (*loc. cit.*), melts at 152°.

The substance hitherto described as α-isofenchonoxime, melting at 113—114°, is, without doubt, *fencholenamide;* it yields fenchonitrile when treated with phosphoric anhydride, and is identical with the product obtained by heating ammonium fencholenate in sealed tubes at 205—210°. It is probable that β-isofenchonoxime is a lactam; it has basic properties, and is formed when fencholenamide is treated with dilute mineral acids.

When fencholenamide is reduced in alcoholic solution with sodium, fencholenic acid and fencholenamine are formed, together with *isofencholenic alcohol*, $C_{10}H_{18}O$, which boils at 218°, and is an unsaturated alcohol; its solution in glacial acetic acid becomes deep red on addition of concentrated sulphuric acid. The sp. gr. = 0·927 at 20°, and the refractive power is $[n]_D = 1·476$, or $M = 47·04$, the calculated value being $M = 47·15$.

Fenchenole, $C_{10}H_{18}O$, is obtained by heating isofencholenic alcohol with dilute sulphuric acid for eight hours in a reflux apparatus; it is isomeric with cineole, which it closely resembles, although it boils at 183—184°. The sp. gr. = 0·925 at 20°, and the refractive power $[n]_D = 1·46108$, or $M = 45·69$, the calculated value for a saturated oxide being $M = 45·61$. The formation of fenchenole affords an interesting parallel with the conversion into oxides of the alcohols

obtained from methyl hexylene ketone and methyl heptylene ketone (Abstr., 1893, i, 597).

The author discusses the behaviour of fenchone and its derivatives, and expresses its constitution by the formula $\begin{matrix}CHMe\cdot CH\cdot CH_2\\ |\quad\quad |\\ CH_2-CH-CO\end{matrix}>CMe_2$.

M. O. F.

Occurrence of Citronellal in Citron Oil. By OSCAR G. DOEBNER (*Arch. Pharm.*, 1894, **232**, 688—691).—The author has obtained the aldehyde citronellal, $C_{10}H_{18}O$, from citron oil as well as the related compound citral, $C_{10}H_{16}O$. These were separated as substituted cinchonic acids, $C_9H_{17}\cdot C_{14}H_8NO_2$ and $C_9H_{15}\cdot C_{14}H_8NO_2$, by digesting the oil with pyruvic acid and β-naphthylamine. The citronellal acid forms crystals which are more easily soluble than those of the citral acid. L. T. T.

Action of Nitrous acid on Amidocamphor. By ANGELO ANGELI (*Gazzetta*, 1894, **24**, ii, 317—325; compare this vol., i, 61).—Azocamphanone yields a *hydrazone* which crystallises in lustrous yellow scales melting at 216°, and when distilled with dilute sulphuric acid gives hydrazine sulphate and "camphadione," $C_8H_{14}<\begin{matrix}CO\\ |\\ CO\end{matrix}$.

Camphenoneoxime in ethereal solution is converted by phosphorus pentachloride into a colourless, crystalline *substance* melting at 87°; this is still under examination. W. J. P.

Bromo-Derivatives of the Camphor Series. By ANGELO ANGELI and E. RIMINI (*Ber.*, 1895, **28**, 819—820).—Camphenone (this vol., i, 61) behaves as an unsaturated compound, decolorises permanganate solution, and is reduced to camphor by nascent hydrogen. It combines with hydrogen bromide to form a substance which melts at 114°, and is isomeric with bromocamphor. Camphenone also combines with bromine to form an oily product which, when treated with alcoholic potash, yields *monobromocamphenone*, $C_{10}H_{13}BrO$; this crystallises well, and melts at 70°.

Monoketazocamphoquinone, $C_{10}H_{14}N_2$, also reacts with bromine, nitrogen being eliminated and an oily product formed. A. H.

Action of Hydroxylamine on Camphoric Anhydride. By GIORGIO ERRERA (*Gazzetta*, 1894, **24**, ii, 336—348).—Sodium ethoxide dissolved in alcohol reacts readily with a boiling alcoholic solution of camphoric anhydride and hydroxylamine hydrochloride yielding a *salt*, $C_{30}H_{44}N_2O_{10}Na_2$, which crystallises in needles on concentrating the solution, and is readily soluble in water; the corresponding *lead* compound, $C_{30}H_{42}N_2O_{10}Pb_2$, is a white powder insoluble in water. The corresponding *acid*, which probably has the constitution

$$OH\cdot N(CO\cdot C_8H_{14}\cdot CO\cdot N(OH)\cdot CO\cdot C_8H_{14}\cdot COOH)_2,$$

cannot be prepared in the free state as its lead salt is decomposed by hydrogen sulphide into camphoric acid and *camphorylhydroxylamine*,

$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>N\cdot OH(?)$. The latter crystallises in lustrous, colourless, orthorhombic needles, melting at 225—226°;

$$a : b : c = 1{\cdot}0472 : 1 : 0{\cdot}5596.$$

Its *sodium* derivative, $C_{10}H_{14}NO_3Na$, crystallises in colourless needles. The hydroxylamine is readily hydrolysed, yielding the corresponding *hydroxamic acid*, $C_8H_{14}<\begin{matrix}CO\cdot NH\cdot OH\\COOH\end{matrix}$, which could not be isolated.

The *copper* salt, $C_8H_{14}<\begin{matrix}CO\cdot NHO\\COO\text{——}\end{matrix}>Cu,2H_2O$, is a green powder, soluble in water; on heating its aqueous solution, an insoluble *monohydrate*, $C_{10}H_{15}NO_4Cu,H_2O$, is deposited. W. J. P.

Action of Potassium Hypobromite on Camphoric Amide. By GIORGIO ERRERA (*Gazzetta*, 1894, **24**, ii, 348—350).—The author employs a slightly modified form of Winzer's method (Abstr., 1890, 1150) for preparing camphoric amide from ethylic camphorylmalonate. On allowing bromine to act on the amide, heat is developed, but no hydrogen bromide is evolved; and on pouring the mixture into potash, a white, crystalline *substance*, $C_{10}H_{16}N_2O_2$, melting at about 235°, separates; it is soluble in bases, alcohol, or water. Its formation is probably due to the conversion of one $CO\cdot NH_2$ group of the amide into an isonitrile group, which then condenses with the other $CO\cdot NH_2$ group; the new substance would thus have the constitution $C_8H_{14}<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}$. W. J. P.

Derivatives of Campholic Acid. By GUERBET (*Bull. Soc. Chim.*, 1894, [3], **11**, 610—618).—*Campholic anhydride*, $(C_{10}H_{17}O)_2O$ (molecular weight by cryoscopic method), is obtained by heating campholic acid with acetic anhydride or chloride, or by the action of campholic chloride on silver campholate. Like its derivatives, it is insoluble in water, but soluble in alcohol, ether, &c., separating from these solvents in large, colourless crystals, or slender needles; it melts at 56°, and boils at 209—210° (20 mm.). Campholic anhydride is slowly hydrolysed to the acid by aqueous or alcoholic potash, and is converted by alcohol into the ethylic salt, and by ammonia into the amide described by Errera (Abstr., 1893, i, 108). The *anilide*, from the anhydride and aniline at 100°, crystallises in long needles, and melts at 91°; it is easily hydrolysed by acids at 150°, but with difficulty by alkalis. The *phenylhydrazide*, prepared by boiling the anhydride with phenylhydrazine, forms nacreous crystals, and melts at 171°. In making campholic chloride from the acid and phosphorus pentachloride, the materials must be perfectly dry, as in presence of phosphoric acid the chloride is decomposed to a large extent into campholene, carbonic anhydride, and hydrogen chloride.

Campholic cyanide, $C_{10}H_{17}O\cdot CN$ (molecular weight by cryoscopic method), prepared from the chloride and silver cyanide at 100°, crystallises from ether in large, white, rectangular plates, and has an odour resembling that of camphor; it melts at 33°, and boils at 227°. It is

readily hydrolysed by alkalis into its proximate constituents; with hydrochloric acid as the hydrolytic agent, the hydrogen cyanide is further hydrolysed into ammonia and carbonic oxide, or in presence of alcohol into ethylic formate.

Dicampholyl, $C_{10}H_{17}O{\cdot}C_{10}H_{17}O$ (molecular weight by cryoscopic method), is formed by the action of sodium on campholic chloride in light petroleum; it forms lemon-yellow crystals, melts at 90°, and boils and decomposes at 330—335°. Dicampholyl is not hydrolysed by alcoholic potash or hydrochloric acid at 150°, nor is it acted on by any of the usual ketonic reagents; nevertheless, it appears to be a ketone, as it is reducible to an alcohol, the ketone being regenerated on treating this with chromic acid.

Dicampholylic alcohol, $C_{10}H_{17}O{\cdot}C_{10}H_{18}{\cdot}OH$, is formed by reducing dicampholyl with moist sodium in ethereal solution; it crystallises in small prismatic plates, and melts at 50°. The *acetate* (molecular weight by cryoscopic method) crystallises in small, colourless needles, and melts at 64°; it is hydrolysed by alcoholic potash into its proximate constituents. Jn. W.

Abietic acid. By Heinrich Mach (*Monatsh.*, 1894, **15**, 627—644; compare Abstr., 1893, i, 582).—The author has previously shown (*loc. cit.*) that the so-called abietic, sylvic, and pimaric acids obtained from the resin of pine trees are one substance, $C_{19}H_{28}O_2$, for which the name abietic acid is retained. It crystallises on slow evaporation of its ethyl alcoholic solution in hemimorphous, monoclinic plates, $a : b : c = 1{\cdot}1866 : 1 : 0{\cdot}9899$, and gives characteristic colour reactions. A solution in dry chloroform when heated with acetic anhydride and sulphuric acid gives a purple-red coloration, which changes through violet and blue to greenish-black (compare Seifert, Abstr., 1891, i, 256, 1894, ii, 469). A solution in sulphuric acid is red. It has a specific rotatory power of $[\alpha]_D = 66{\cdot}66$, and gives a *potassium salt*, $C_{19}H_{27}O_2K$, which crystallises in silky needles; an amorphous, white, *barium salt*, $(C_{19}H_{27}O_2)_2Ba$, which becomes yellow on exposure to air, and an *acid ammonium salt*,

$$C_{19}H_{27}O_2NH_4,C_{19}H_{28}O_2,$$

which is very soluble and crystallises in drusy masses of prisms. On oxidation with potassium permanganate in alkaline solution, an *acid* having the formula $C_{10}H_{16}O_3$ and melting at 123° is obtained. On oxidation with bromine water, abietic acid yields an amorphous substance which has the formula $C_{10}H_{10}O_4$, turns brown at 130°, and melts and decomposes at 137°.

Abietic acid is neither identical nor isomeric with Maly's pimaric acid, $C_{20}H_{30}O_2$, obtained from *Gallipot* and *Colophonium de Bordeaux*. The so-called metacopaivic acid appears to have the formula $C_{15}H_{23}{\cdot}OH$, and is possibly the root of the cholesterol series. On this account the author proposes to name it *metacholestol*. G. T. M.

Amber (Succinite). By Alexander Tschirch and E. Aweng (*Arch. Pharm.*, 1894, **232**, 660—688).—The authors find that the portion of succinite soluble in alcohol consists principally (28 per cent. of the weight of the succinite) of *succinoabietic acid*, $C_{60}H_{120}O_5$,

together with a small quantity (2 per cent.) of the borneol salt of this acid, and some sulphur. The portion (70 per cent.) of succinite insoluble in alcohol (succinin) is almost entirely composed of the succinate of a resin-alcohol to which the authors give the name *succinoresinol*. Succinoabietic acid is crystalline, soluble in alcohol and ether, insoluble in water, and melts at 148°. It forms a monacetyl derivative, but could not be further acetylated. When digested with alcoholic potash, it is decomposed, yielding *succinosilvic acid*, $C_{20}H_{30}O_2$, and *succinoabietol*, $C_{40}H_{60}O_2$. Succinosilvic acid is easily soluble in alcohol, ether, and glacial acetic acid, but could not be obtained in a crystalline form. It yields a white, amorphous silver salt. Succinoabietol is readily soluble in alcohol, ether, and chloroform, insoluble in light petroleum. It forms a triacetate, soluble in light petroleum. Succinoabietic acid, when fused with potash at a moderate heat, yields succinic acid. *Succinoresinol*, $C_{12}H_{20}O$, is a white amorphous powder soluble in a mixture of alcohol and ether and melting at 275°. It yields an *acetyl derivative* as a granular resin, soluble in alcohol and in ether.

Gedanite appears to be similar in composition to succinite, except that it is free from sulphur. It is apparently the presence of the sulphur which causes in succinite the increase of melting point, elasticity and tenacity.

Glessite contains succinoabietic acid and a succinin or a very similar compound, but was not further investigated. In it borneol seems to be replaced by a compound resembling carvol.

Allingite differs considerably from the other members of the amber group, and contains neither borneol nor succinic acid. The resin-acid also appears not to be succinoabietic acid. L. T. T.

Commercial Thapsia Resin. By Francesco Canzoneri (*Gazzetta*, 1894, **24**, ii, 437—438).—The author has isolated the following substances from commercial thapsia resin: cholesterol, isocholesterol, thapsic acid, a terpene, a camphor, angelic acid, isovaleric acid, caproic acid, caprylic acid, euphorbion, a greenish aromatic oil, a resin containing sulphur and waxy, gummy, and fatty matters, &c.; a small proportion of a *substance* which induces frothing and melts at 87° was also separated. The cholesterol, euphorbion, and the terpene were not found during the author's previous examination of thapsia resin (*Gazzetta*, **13**, 514), and their presence is probably due to adulteration.

W. J. P.

Sap of the Lac Tree. By Gabriel Bertrand (*Bull. Soc. Chim.*, 1894, [3], **11**, 717—721).—The sap of the Tonquin lac tree (*Rhus succedanea*, Linn.), which forms the basis of various kinds of lacquer, is a thick, nearly white, alkaline cream, superficially oxidisable by air to an intensely black, impervious substance, insoluble in the usual solvents.

Complete oxidation only takes place in the presence of a diastatic ferment, *laccase*, which can be separated from the other essential constituent of the sap by means of alcohol, in which it is insoluble. When precipitated by alcohol from aqueous solution, the crude laccase dries to white, opaque fragments, like gum, and is probably a mixture

of the ferment with carbohydrates, as it can be oxidised to mucic acid, and hydrolysed to galactose and arabinose.

From the portion of the sap soluble in alcohol, a substance, *laccol*, probably a polyphenol, can be precipitated by lead acetate. It is a thick oil, insoluble in water, but soluble in alcohol, &c., and is intensely irritating to the skin, as is the crude sap. Laccol is readily oxidisable in the air to a reddish, viscous, or resinous substance; in alkaline solution, it behaves like pyrogallol, blackening, and absorbing oxygen with such rapidity as to become hot; it reduces ferric chloride in alcoholic solution, forming a black, metallic derivative.

When laccol is precipitated from alcoholic solution by an aqueous solution of laccase, the white emulsion rapidly blackens from absorption of oxygen; but this does not take place if the laccase solution has been boiled, or if water alone is the precipitant. The action of laccase on gallic acid, pyrogallol, &c., is similar, the rate of absorption of oxygen being enormously increased. As the ferment has no action on starch, sugar, amygdalin, &c., it seems to be the first member of a new class of "oxidising diastases." It is probably widely distributed through the vegetable kingdom, as the author has already detected it in gum senegal and gum arabic. JN. W.

Laccase, an Oxidising Diastase. By GABRIEL BERTRAND (*Compt. rend.*, 1895, **120**, 266—269).—The author has previously shown that the conversion of the milky juice of the lac tree into a black varnish depends partly on the action of a diastase, *laccase*, which he regarded as having hydrolysing powers analogous to those of other diastases (preceding abstract). He finds, however, that the laccol in the juice absorbs oxygen much more rapidly in presence of the diastase than under ordinary conditions. It seems, therefore, that laccase has the power of promoting oxidation, and this is confirmed by the fact that a sterilised solution of quinol containing laccase, prepared aseptically, rapidly absorbs oxygen from the air with formation of quinone and quinhydrone, although in the absence of laccase, or in presence of laccase that has been boiled for a short time, no absorption of oxygen takes place even after several days.

Pyrogallol solution in presence of laccase behaves similarly, and purpurogallin is formed, carbonic anhydride being evolved. Gallic acid and tannin are also oxidised, with liberation of carbonic anhydride. Since laccase is present in many plants, it seems not improbable that this diastase plays an important part in the respiration of plants. In the author's experiments precautions were taken to prevent the possible presence of micro-organisms. C. H. B.

Oxidation of the Tannin of Cider Apples. By LÉON LINDET (*Compt. rend.*, 1895, **120**, 370—372).—The author has previously observed that the conditions necessary for the oxidation of the tannin of cider apples coincide with those necessary for the existence of a soluble ferment, and he concluded that a soluble ferment takes part in the oxidation (*Le Cidre*, 1893, 150). Bertrand's observations on laccase (preceding abstract) suggested that a similar diastase might be present in cider apples. When sliced or

pulped apples, or sponges moistened with the juice, are exposed to air, there is absorption of oxygen and liberation of carbonic anhydride, even if the sponges have been sterilised and the juice has been filtered through biscuit porcelain, or if oil of mustard is added. Salicylic acid and other antiseptics retard the oxidation, and chloroform and mercury compounds have the same effect, but they are known to behave similarly with diastases. The rate of oxidation varies with the alkalinity or acidity of the juice. No oxidation takes place with juice that has been boiled, and it is well known that cooked apples do not become red on exposure to air.

If apple juice is mixed with alcohol and the precipitate is suspended in water, it will cause oxidation of boiled juice. Further proof that alcohol precipitates the soluble ferment lies in the fact that apples from which the air has been pumped, and which have been crushed in alcohol, yield a juice which does not oxidise on exposure.

Apple juice causes the oxidation of pyrogallol to purpurogallin, but the boiled juice has not this effect.

All these facts indicate that apples contain a soluble diastase, probably a laccase, to which the oxidation on exposure to air is due; but whether the laccase acts directly, or whether it splits up the tannins into more readily oxidisable substances, has yet to be determined. The laccase is intimately associated with the tannins, and cannot be removed by merely washing with boiled water.

C. H. B.

Quercetin Derivatives. By JOSEF HERZIG (*Monatsh.*, 1894, **15**, 683—699; compare Abstract, 1888, 1309; 1890, 64; 1891, 1386; 1893, i, 413).—By the interaction of bromine and quercetin, Liebermann and Hamburger obtained a substance which they regarded as a tribromoquercetin. The author now shows that the numbers obtained by those investigators and by himself correspond much more closely with the formula for dibromoquercetin, $C_{15}H_8Br_2O_7$, but that the substance, on purification by recrystallisation, gradually loses bromine (compare Herzig and Pollak, this vol., i, 343). *Tetrethyldibromoquercetin*, obtained on bromination of tetrethylquercetin, is, on the other hand, a very stable compound, and therefore contains the bromine in the closed chain. It crystallises in yellow needles, melts at 169—173°, and does not exchange its hydroxyl groups for acetyl when heated with acetic anhydride and sodium acetate.

From the results of earlier investigations, the author regards quercetin as hydroxyfisetol, and rhamnetin as a monomethyl derivative of quercetin. Since the groups

$$C_6H_3(OH)_2\cdot CO- \text{ and } OH\cdot C_6H_3\cdot(CO\cdot CH_2\cdot OH)\cdot O-$$

have been recognised in decomposition products of fisetol, that substance may be regarded as being formed from them by elimination of water, and as having the constitution

$$\begin{array}{l} HO\cdot C{:}CH\cdot C\cdot CO\cdot C\cdot C_6H_3(OH)_2 \\ \quad\quad\quad\

between fisetol and catechol is further shown by the production of diethylprotocatechuic acid and ethylresorcylglyoxylic acid,

$$[CO{\cdot}COOH : OH : OEt = 1 : 2 : 4],$$

when ethylfisetol is oxidised with potassium permanganate.

G. T. M.

Sordidin. By EMANUELE PATERNÒ and F. CROSA (*Gazzetta*, 1894, **24**, ii, 325—335).—The ethereal extract from *Zeora sulphurea* is a mixture of sordidin, the substance $C_{27}H_{30}O_9$, usnic acid, and rangiformic acid (Abstr., 1894, i, 541). Sordidin, $C_{13}H_{10}O_8$, which Paternò first isolated from *Zeora sordida* (*Gazzetta*, **6**, 129), has the normal molecular weight in boiling benzene, crystallises in slender, monosymmetric needles melting at 209—210°, and is optically inactive in solution; when boiled with alkalis, it yields a small quantity of a white crystalline *acid* melting at 183—184°. Acetic anhydride converts it into a *polymeride*, $(C_{13}H_{10}O_8)_3$, of which the molecular weight was determined by Beckmann's method, and which forms small, white, anorthic crystals melting at 236—237°; a small quantity of an *acetyl* derivative melting at about 198—200° is obtained at the same time, but could not be satisfactorily purified. The *benzoyl* derivative, $C_{13}H_9O_8Bz$, melts at 222—223°, but could not be obtained pure owing to its admixture with the polymeride of sordidin described above; the acid melting at 184° is obtained on treating the above benzoyl derivative, or the polymeride, with sodium ethoxide.

Sordidin is reduced by sodium amalgam in acetic acid solution with formation of a *substance*, $C_{15}H_{12}O_9$, which crystallises in flexible, white needles melting at 180—181°; the *acetyl* derivative, $C_{15}H_{11}O_9Ac$, forms lamellar crystals melting at 149—150°. This reduction product is accompanied by a *compound* crystallising in hard, red prisms melting at 277°.

Analyses and molecular weight determinations in boiling benzene show that the acid obtained by treating sordidin with sodium ethoxide has the composition $C_{26}H_{28}O_{16}$; it crystallises in colourless needles melting at 182—183°, and decomposes carbonates. No oxidation products of interest were obtained either from sordidin or from this compound; the former is shown by Zeisel's method to contain one methoxy-group.

W. J. P.

Scarlet acid. By CARL BÖTTINGER (*Arch. Pharm.*, 1894, **232**, 698—704).—When thiocarbamide (6 grams) is rubbed in a mortar with glyoxylic acid (6·6 grams), a slight evolution of gas occurs, and a white salt is first produced which, however, rapidly changes to a tenacious, pasty mass. The colour changes first to yellow and then to red. *Scarlet acid*, $C_4H_6N_4S_2O$, when isolated from the products of the reaction, is a scarlet powder sparingly soluble in alcohol, ether, acetone, and cold water. It is sparingly soluble in hydrochloric acid, but readily soluble in sulphuric acid forming a brownish-yellow solution, which decomposes when heated. The sodium and ammonium salts have a very intense yellowish-red colour. The aluminum and lead salts form cherry-red precipitates; the silver salt a purple precipitate which gradually darkens. When the solutions of the alkali salts are boiled, the acid is decomposed, thiocarbamide being formed, ammonia

evolved, and a new substance left which is sometimes yellow and sometimes red, but yields colourless alkali salts. L. T. T.

Chlorophylls from Lucern. By ALEXANDRE L. ÉTARD (*Compt. rend.*, 1895, **120**, 328—331).—The author has already described one form of chlorophyll, α-medicagophyll, from lucern (this vol., i, 66—67), and has shown that many of the substances commonly called chlorophylls are very complex mixtures. Chlorophylls dissolved in fused potash or in concentrated sulphuric acid are converted into brown colouring matters, which when precipitated and redissolved, although no longer green, retain the red fluorescence and the absorption characteristics of chlorophyll, and hence it would seem that there exists in plants a very stable nucleus to which various molecular groups become attached, with formation of the various chlorophylls, these rapidly undergoing chemical changes under the influence of light.

Leaves of lucern which have been exhausted with carbon bisulphide (*loc. cit.*), if treated with hot alcohol, yield a green mass; this, when separated from the brown extracts, dissolves in a small quantity of alcohol of 90°, and, after this solvent has been removed, leaves a residue which is completely soluble in ether, and therefore contains no gums, tannins, vegetable acids, &c. The product is next extracted with pentane, and the residue is treated with ether, by which it seems to be partially decomposed, a brown residue being left, whilst a green chlorophyll, *β-medicagophyll*, dissolves. It has a peculiar odour, and when dried is a green solid with a vitreous, conchoidal fracture. It is insoluble in and heavier than water, with which, however, it forms an emulsion; it dissolves immediately in dilute aqueous potash, but is reprecipitated by sodium chloride and also by acids. It reduces ammoniosilver nitrate in presence of potassium hydroxide, with production of a mirror, and hence would seem to have an aldehydic function or to be a readily decomposable glucoside.

β-Medicagophyll has the composition $C_{42}H_{63}NO_{14}$, and is much more abundant in lucern than α-medicagophyll. C. H. B.

Chlorophylls. By ARMAND GAUTIER (*Compt. rend.*, 1895, **120**, 355—356).—A question of priority. In 1877, the author showed that the chlorophyll from spinach differs from that of other plants, and notably from that of the *graminæ* in the low proportion of nitrogen and the high proportion of oxygen which it contains. It is crystallisable, contains no iron, but contains phosphorus and magnesium. In 1886, he showed that the chlorophyll from rye-grass has the composition $C_{30}H_{48}N_2O_3$, and that from spinach $C_{40}H_{64}N_2O_4$; and this latter formula he now confirms. He also found that the chlorophyll of the male fern is remarkably sensitive to the oxygen of the air under the influence of light. Algæ, fucus, and probably some higher plants contain brown, yellow, and red pigments which behave like chlorophylls, and have the power of decomposing the system $CO_2 + H_2O$, with liberation of oxygen. C. H. B.

Protophyllin, Natural and Artificial. By CLEMENZ A. TIMIRIAZEFF (*Compt. rend.*, 1895, **120**, 467—470).—The *protochlorophyll*

described by Monteverde in a recent number of *Acta Horti Petropolitani* is identical with the protophyllin described by the author, who also showed that there is no difference between the protophyllin prepared by reduction and that existing in etiolated plants (Abstr., 1886, 626, and 1889, 1236). C. H. B.

Compound of Pyrroline with Hydroferrocyanic acid. By Carlo U. Zanetti (*Gazzetta*, 1894, **24**, ii, 373—375; compare Ciamician and Zanetti, Abstr., 1893, i, 602).—Details are given of the preparation of pyrroline ferrocyanide by the action of a hydrochloric acid solution of potassium ferrocyanide on pyrroline at a low temperature; the substance cannot be crystallised from water or alcohol, in which it dissolves, as it decomposes on heating. It is decomposed by light or by contact with air, and is converted by potash into a caseous mass. W. J. P.

Coal-tar Bases. By Felix B. Ahrens (*Ber.*, 1895, **28**, 795—798).—The light oil from 10,000 kilos. of coal-tar was shaken with dilute sulphuric acid, and 5 kilos. of bases were so obtained. These consisted of pyridine, picoline, and lutidine, together with a fraction (400 c.c.) boiling at 160—220°; this last fraction was freed from aniline by oxidising the latter to aniline black, and was then carefully fractionated, the three fractions mentioned below being further examined. (I), boiling at 165—170°, consisted mainly of 2 : 4-dimethylpyridine, together with a little symmetrical trimethylpyridine, and a hitherto unknown collidine, the *platinochloride* of which, with $2H_2O$, darkens at 210°, decomposing finally at 255°, whilst the *aurochloride* crystallises in long needles, which, if left in the solution, change to rhomboidal crystals; it melts at 237—238°. (II), boiling at 170—180°, is mainly symmetrical trimethylpyridine. (III), boiling at 220—230°, yields a parvoline boiling at 232—234 (corr.), probably identical with the substances obtained by Greville Williams (this Journal, 1854, 97) out of the oil from Dorsetshire bituminous shale, and by Thenius (*ibid.*, 1861, 502) from coal-tar oil. It is shown to be 2 : 3 : 4 : 5-*tetramethylpyridine*, being identified by means of the tetracarboxylic acid that it yields when oxidised with permanganate; the isomeride obtained from propaldehyde-ammonia by Dürrkopf and Göttsch (Abstr., 1890, 1002, where *for* [$Me_4 = 1 : 2 : 3 : 4$] *read* [$Me_4 = 2 : 3 : 4 : 5$]) must therefore have another constitution. The base is a colourless liquid, slightly soluble in water; the *platinochloride* melts and decomposes at 209—210°; the yellow *aurochloride* softens at 212°, and melts at 216—218°; the *mercurichloride* melts at 156°, and the picrate at 170—172°. C. F. B.

Lead Double Salts with Organic Bases. By Wm. Goebbels (*Ber.*, 1895, **28**, 792—794; compare Classen and Zahorski, Abstr., 1893, 464, and Friedrich, *ibid.*, 415).—Lead tetrachloride forms a yellow, crystalline, double compound, $3PbCl_4,7(C_6NH_7,HCl)$, with picoline hydrochloride; this compound dissolves in water, but lead dioxide soon separates out from the solution. It also forms a compound $PbCl_4,2(C_7NH_9,HCl)$, melting at 135°, with lutidine hydrochloride; if

excess of the latter is present a yellow crystalline compound, $2PbCl_4,5(C_7NH_9,HCl)$, melting at 132°, is obtained. A compound is also formed with collidine hydrochloride.

Lead dichloride unites with picoline hydrochloride to form lustrous white plates of a compound $2PbCl_2,C_6NH_7,HCl$, which decomposes at 80—90°; with lutidine hydrochloride it unites to form a white, crystalline compound, $2PbCl_2,C_7NH_9,HCl$. Lead bromide unites with pyridine, forming a compound $PbBr_2,C_5NH_5$, which crystallises in needles. When allowed to remain in contact with pyridine, these change to rhombohedra of a compound $5PbBr_2,7C_5NH_5$. Lead iodide forms with quinoline, pale yellow needles, with the composition $PbI_2,2C_9NH_7$. C. F. B.

Ethylic Nicotinate and β-Amidopyridine. By Felix Pollak (*Monatsh.*, 1895, **16**, 45—61).—Ethylic nicotinate, $C_8H_9NO_2$, obtained by Engler's method (Abstr., 1894, i, 472), boils at 224° (6° higher than is given by Engler), and forms the following salts:—A *hydrochloride*, $C_8H_9NO_2,HCl$, which crystallises in deliquescent needles and melts at 118—120°; a *platinochloride*, $C_8H_9NO_2,H_2PtCl_6$, which crystallises in yellow needles and melts at 161°; an *aurochloride*,

$$C_8H_9NO_2,HAuCl_4,$$

which crystallises in light yellow scales and melts at 117°; and a readily soluble *ethiodide*. The last-named forms a *platinochloride*, $(C_8H_9NO_2Et)_2PtCl_6$, which crystallises in small plates and melts at 176°; and an *aurochloride*, $C_8H_9NO_2Et,AuCl_4$, which crystallises in light yellow scales, melts at 59°, and is converted by silver oxide into the *ethylbetaïne* of *nicotinic acid*. This forms hygroscopic crystals, melts at 84—86°, and yields a *platinochloride*, $(C_8H_9NO_2)_2,H_2PtCl_6$, which crystallises in bright yellow needles, and melts at 205°.

On heating ethylic nicotinate with alcoholic ammonia saturated at −10°, for 12 hours at 150°, it is converted into *nicotinamide*, which melts at 121° (Engler gives 125° as the melting point), and with potassium hypobromite yields *β-amidopyridine*, $C_5H_6N_2$. The latter crystallises from a mixture of benzene and light petroleum, melts at 64°, boils at 250—252°, dissolves readily in water, alcohol, ether, and benzene, and forms a *hydrochloride*, $C_5H_6N_2,2HCl$, which crystallises in plates and melts at 175°; a *platinochloride*, $(C_5H_6N_2)_2,H_2PtCl_6$, which melts and decomposes at 225°, and an *aurochloride*, $C_5H_6N_2,HAuCl_4$, which crystallises in dark-red needles and decomposes and evolves gas at 218°. On the addition of potassium nitrite to a solution of β-amidopyridine in dilute sulphuric acid, *β-hydroxypyridine*, which melts at 126·5°, is obtained.

In the preparation of β-amidopyridine, a substance which melts at 100°, contains bromine, and is probably *bromamidopyridine*, is formed as a bye-product. If a relatively small quantity of potash is used in the preparation, less amidopyridine is formed, and the liquid, on shaking with ether, yields a substance which crystallises in scales, melts at 129—131°, has an odour of iodoform, and is isomeric with nicotinamide. G. T. M.

Quinoline in Brown-coal Tar. By Oscar G. Doebner (*Arch. Pharm.*, 1894, **232**, 691—693).—The author has isolated quinoline from the fraction of brown-coal tar boiling at 240—245°. Other quinoline and pyridine derivatives are also present. L. T. T.

2 : 4-Dichloroquinoline. By Adolph Claus and Alfred Ammelburg (*J. pr. Chem.*, 1895, [2], **51**, 415—422; compare Abstr., 1894, i, 473, 553).—2 : 4-Dichloroquinoline is prepared by the usual method from 3 : 5-dichloraniline; it crystallises in colourless, lustrous prisms or aggregates of needles, melts at 116—117°, and sublimes in needles. Its salts are prepared by dissolving it in strong acids; the *hydrochloride* melts at 216°, and the anhydrous *sulphate* at 162°; the *dichromate* melts and decomposes at 159°; the *platinochloride* is described; the *methiodide* melts at 255—257°; the *methochloride* and its *platinochloride* were prepared.

1 : 2 : 4-*Nitrodichloroquinoline* crystallises in tablets or prisms, melts at 168·5°, and dissolves freely in ether and chloroform, but only sparingly in cold alcohol; no salts and no methiodide can be prepared; the *platinochloride* decomposes and melts at 255°. The corresponding *amido*-derivative crystallises in brilliant, colourless prisms, which speedily become coloured on exposure to light; it melts at 125°, and dissolves freely in alcohol, ether, and chloroform; its *hydrochloride*, $C_9NH_4Cl_2{\cdot}NH_2,HCl$, forms red needles, melts and decomposes at 183°, and is dissociated by water; the *platinochloride* and *methiodide* (m. p. 154°) are described.

By diazotising the above amidodichloroquinoline, 1 : 2 : 4-*trichloroquinoline* is obtained; this crystallises in prisms and melts at 150°. A. G. B.

Constitution of the Hydroquinolines. By Giacomo Ciamician and G. Boeris (*Gazzetta*, 1894, **24**, ii, 299—310).—The indolic properties of dihydrotrimethylquinoline (Ferratini, Abstr., 1894, i, 96) are shown by the behaviour of its acetyl derivative towards benzaldehyde; a *cinnamoyldihydrotrimethylquinoline*, $C_{21}H_{21}NO$, is thus obtained, which crystallises in beautiful, orange-yellow, rectangular plates melting at 152—153°, and dissolves in most organic solvents.

On distilling dihydrotrimethylquinoline hydriodide, a mixture of methylic iodide, trimethylindole and dihydrotrimethylquinoline is obtained; the latter crystallises in the orthorhombic system, $a : b : c = 1{\cdot}3558 : 1 : 0{\cdot}5984$. Trimethylindole is readily converted into dihydrotrimethylquinoline hydriodide by heating with methylic iodide at 100°.

A discussion of the constitutions of the quinolines and indoles is given. W. J. P.

Action of Phosphoric Anhydride on Benzylideneacetoneoxime. By Carl Goldschmidt (*Ber.*, 1895, **28**, 818—819).—Benzylideneacetoneoxime, when mixed with infusorial earth and treated with phosphoric anhydride, yields isoquinoline. It appears therefore that, as in the case of cinnamaldehyde (Abstr., 1894, i, 552), intramolecular change occurs. A. H.

Cyanide and Carboxylic acid Derived from Isoquinoline. By BERTHOLD JEITELES (*Monatsh.*, 1894, **15**, 807—820).—*Cyanoisoquinoline* is obtained on distilling in a stream of hydrogen a mixture of the dried sodium salt of Hoogewerff and van Dorp's isoquinolinemonosulphonic acid with potassium ferrocyanide. It crystallises from water in yellow needles, melts at 135°, and, when heated with hydrochloric acid at 150—160°, yields the *hydrochloride* of *isoquinolinecarboxylic acid*, $C_9NH_6{\cdot}COOH,HCl + 2H_2O$. The latter crystallises in needles and forms a red solution, which shows a green fluorescence. The free acid, $C_{10}H_7NO_2$, is sparingly soluble in water, crystallises in yellow needles, commences to blacken at 247—250°, and melts at 272°. The *nitrate* crystallises in needles, gives a yellow solution showing a green fluorescence, and melts and decomposes at 218—220°. The *picrate* melts at 212—213°.

On oxidation in neutral solution with potassium permanganate, isoquinolinecarboxylic acid is converted into hemimellitic acid. The carboxyl group is therefore in the *ortho*- or *ana*-position.

G. T. M.

β-Cyano-γ-phenylpseudocarbostyril. By ICILIO GUARESCHI (*Chem. Centr.*, 1894, ii, 211).—*β-Cyano-γ-phenylpseudocarbostyril*, $NH<\begin{matrix}C_6H_4{\cdot}CPh\\ \|\\ CO-C{\cdot}CN\end{matrix}$, is obtained by the action of ethylic cyanacetate on orthamidobenzophenone; it forms colourless needles, melts at 267°, and volatilises and sublimes at a higher temperature; it is isomeric with Gabriel and Neumann's 3 : 4-phenylcyanisocarbostyril.

D. A. L.

Hydroxamic Acids and Hydroxyfurfurazane Derivatives. By ARTHUR HANTZSCH and J. URBAHN (*Ber.*, 1895, **28**, 753—766; compare Abstr., 1894, i, 274).—Ethylic succinate and hydroxylamine, in presence of alkalis or ammonia, react, succinamide and succinaminehydroxyamic acid being formed; the latter could not be isolated on account of its great solubility, but was recognised by means of the ferric chloride reaction, and the production of the *tetracetate*, $C_2H_4[C(OAc):NOAc]_2$, which crystallises in long needles and melts at 130°. *Oxaldihydroxamic tetracetate*, $OAc{\cdot}N:C(OAc){\cdot}C(OAc):N{\cdot}OAc$, crystallises in cubical crystals, melts at 141°, and resembles the preceding compound. *Malondihydroxamic* acid forms an acetate with difficulty; it melts at 65—67°, and was only obtained in small quantity.

Ammonium oxazolonehydroxamate, $CO<\begin{matrix}CH_2{\cdot}C{\cdot}C(OH):N{\cdot}OH,NH_3\\ \|\\ O-N\end{matrix}$, is prepared from ethylic oxalate, hydroxylamine, and ammonia; it crystallises in long prisms, melts and decomposes at 156—160°, and is very readily soluble. The recently prepared salt is neutral, but speedily becomes slightly acid; it becomes successively yellow and red in air, gives a deep red coloration with ferric chloride, and reduces alkaline silver solutions but not Fehling's solution. The *copper salt* is green; the *silver salt* yellow; both these and the *lead salt* dissolve in acetic acid. The acid could not be isolated. Cyanoximidoacetic

acid, $CN\cdot C(NOH)\cdot COOH,\frac{1}{2}H_2O$, is prepared by the action of nitrous acid on the preceding compound, and has been previously obtained by Wolff; it gives a yellow, not red, coloration with ferric chloride.

Hydroxyfurazaneacetic acid, $O<\begin{matrix}N:C\cdot OH\\ N:C\cdot CH_2\cdot COOH\end{matrix}$, is formed by heating ammonium oxazolonehydroxamate with alkali, or directly from ethylic oxalate, hydroxylamine, and soda; it crystallises in colourless prisms or plates, and melts at 158°. The yield is 25 per cent. of the ethylic oxalate employed. The acid is bibasic, does not reduce ammoniacal silver solution, gives a yellow coloration with ferric chloride, and is extremely stable; its molecular weight was determined cryoscopically and by the boiling point method. The *ammonium* salt, $C_4H_1N_2O_4,2NH_3$, crystallises in short, truncated prisms, and melts and decomposes at 174°. The *calcium* salt, $C_4H_2N_2O_4Ca + H_2O$, crystallises in rhombic prisms. The *silver* and *lead* salts are sparingly soluble, the former is crystalline and explodes when heated; the *chloride* has also been prepared.

Hydroxyfurazanecarboxylic acid, $O<\begin{matrix}N:C\cdot OH\\ N:C\cdot COOH\end{matrix}$, is prepared by the oxidation of hydroxyfurazanacetic acid with potassium permanganate in alkaline solution; it crystallises in prisms, melts at 175°, has no action on ferric chloride at ordinary temperatures, but when previously warmed with alkali gives a red coloration indicating a resolution of the closed chain. The acid is stable towards hydrochloric acid; with potassium permanganate in acid solution, cyanacetic acid is formed. The *ammonium* salt, $C_3N_2O_4(NH_4)_2$, crystallises in hexagonal needles, and melts at about 195°. The *barium* salt, $C_3N_2O_4Ba$, is very sparingly soluble, and melts and decomposes above 200°.

Hydroxyimidopropionamide, $NOH:CMe\cdot CO\cdot NH_2$, is formed from ethylic pyruvate, hydroxylamine, and ammonia. Ethylic pyruvate (1 mol.) and hydroxylamine (2 mols.) yield ethylic hydroxyimidopropionate, which, like the amide, gives no coloration with ferric chloride; when boiled with an alkali, hydroxyimidopropiohydroxamic acid is formed; further boiling alone or with an alkali yields only hydroxyimidopropionic acid. J. B. T.

Antipyrine. By Friedrich Stolz (*Ber.*, 1895, **28**, 623—634).—This paper is devoted to a detailed criticism of v. Rothenburg's reasons for regarding 1 : 3-phenylpyrazolone, which melts at 154°, as the 1 : 5-derivative (this vol., i, 303), a view which the author holds to be erroneous.

1 : 5-*Phenylpyrazolidone*, $CO<\begin{matrix}NPh\cdot NH\\ CH_2-CH_2\end{matrix}$, is obtained by the action of ethylic β-iodopropionate on sodium formylphenylhydrazine dissolved in xylene, and subsequent hydrolysis of the product (German Patent, 74,858); it melts at 78° (compare Abstr., 1894, i, 145). The calculated quantity of ferric chloride converts it into 1 : 5-phenylpyrazolone, whilst excess of the reagent gives rise to pyrazolone blue.

Benzylidene-bis-3 : 1 : 5-*methylphenylpyrazolone* is obtained by heating a mixture of methylphenylpyrazolone and benzaldehyde with alcoholic hydrochloric acid; it forms lustrous crystals, and melts at 248°. The action of diazobenzene chloride converts it into 3 : 1 : 4-methylphenylbenzeneazopyrazolone, which melts at 155°.

Ethylic bis-1 : 5-*phenylpyrazolone*-4-*β*-*propionate*,

$$CH(C_3N_2H_2OPh)_2{\cdot}CH_2{\cdot}COOEt,$$

is obtained by heating the hydrazone of ethylic formylacetate with toluene (German Patent, 55,117); it melts at 173—174°. The *platinochloride* is crystalline. The *acid* is formed when the ethylic salt is hydrolysed.

Ethylic 3 : 5 : 1-dimethylphenylpyrazole-4-carboxylate is obtained by the action of acetic chloride on the hydrazone of ethylic acetoacetate and subsequent treatment of the product with alcoholic potash. It melts at 196—198°, and the ethylic salt is identical with Walker's 5 : 3 : 1-ethoxymethylphenylpyrazole. When this method of preparation is adopted, 3 : 1 : 5-methylphenylpyrazolone is formed at the same time. M. O. F.

Constitution of the Phenylpyrazoles. By Ludwig Knorr (*Ber.*, 1895, **28**, 688—696).—The author maintains, in reply to the criticism of Rothenburg (this vol., i, 303) and Buchner (this vol., i, 192), that the phenylpyrazole melting at 78° is the 3- or 5-compound. The derivative melting at 228°, on the other hand, is the 4-compound. Rothenburg's statement that this substance is formed by the action of hydrazine hydrate on benzoylaldehyde is inaccurate, the sole product of the reaction being the phenylpyrazole which melts at 78° (see following abstract). The constitution of 4-phenylpyrazole is proved by the fact that it can be synthetically prepared by a method which admits of no doubt as to the constitution of the resulting pyrazole (next page). Attempts to prepare 4-phenylpyrazole by other methods failed. Ethylic oxalate condenses with benzyl methyl ketone to form *phenyldiketopentoic acid*, $COOH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2Ph$, which is converted by hydrazine hydrate into 3 : 5-benzylpyrazolecarboxylic acid, and does not form the wished for isomeride, $COMe{\cdot}CHPh{\cdot}CO{\cdot}COOH$, from which a 4-substituted phenylpyrazole derivative might have been obtained. It was also found impossible to prepare a pure 4-pyrazolecarboxylic acid from 4-nitropyrazole by means of the diazo-reaction.

A. H.

Condensation of Benzoylaldehyde with Hydrazine. By Ludwig Knorr (*Ber.*, 1895, **28**, 696—698; compare foregoing abstract).—A careful examination of the reaction between benzoylaldehyde and hydrazine shows that the product consists entirely of the phenylpyrazole, which melts at 78°, and is, according to the author, the 3- or 5-derivative. Rothenburg's statement that the pyrazole which melts at 228° is thus formed, is therefore inaccurate. A number of new derivatives of the compound has also been prepared. The *picrate* melts at 170—171°. The *carbamide* crystallises

in needles, and melts at 137—139°. 4-*Bromophenylpyrazole* melts at 116—117°. *Nitrophenylpyrazole* melts at 192—193°. 1-*Methylphenylpyrazole* boils at 280—281°, and forms a *picrate*, which melts at 130—132°, and a *platinochloride*, which crystallises in plates melting at 190°. The *methiodide* of the same base melts at 156—157°, whilst the *platinochloride* of the corresponding methochloride forms orange-coloured prisms, and decomposes at 224°. A. H.

Formation of 4-Phenylpyrazole. By LUDWIG KNORR (*Ber.*, 1895, **28**, 699—701; compare preceding page).—Isopropyl benzyl ketone readily condenses with ethylic formate to produce *hydroxymethylenebenzyl isopropyl ketone*, $CHMe_2{\cdot}CO{\cdot}CPh{:}CH{\cdot}OH$, which is a colourless oil. When treated with hydrazine hydrate in ethereal solution, 3 : 4-*isopropylphenylpyrazole* is formed, which melts at 99—100°; the *hydrochloride* decomposes at 214—215°. On oxidation, 4 : 3-*phenylpyrazolecarboxylic acid* is formed; this crystallises in lustrous plates, and melts and loses carbonic anhydride at 253—254°. It is accompanied by a small amount of *phenylpyrazoledimethylcarbinol*, $CH\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}NH{:}N\\ CPh\end{matrix}\begin{matrix}>\\ \\ \end{matrix}C{\cdot}CMe_2{\cdot}OH$, which melts at 129—130°.

4-Phenylpyrazole is formed when the carboxylic acid is heated at 270°. The substance thus obtained melts at 228°, and is identical with the compound described by Buchner. A. H.

Constitution of Phenylpyrazolone. By LUDWIG KNORR (*Ber.*, 1895, **28**, 701—705; compare the following abstract).—The substance described by Walker (Abstr., 1894, i, 475) as 5 : 3 : 1-ethoxymethylphenylpyrazole is probably identical with ethylic 3 : 5 : 1-dimethylphenylpyrazole-4-carboxylate, previously described by the author (Abstr., 1887, 678), whilst Walker's hydroxymethylphenylpyrazole, obtained by hydrolysis from the first compound, is the corresponding free acid. This removes the ground upon which Rothenburg has founded his criticism of the author's view that the phenylpyrazolone melting at 118° is the 1 : 5-compound. The formulæ proposed by Rothenburg for the isomeric benzoyl derivatives of the technical pyrazolone are also inaccurate. A. H.

Derivatives of the Phenol-form of 3 : 1-Ethylphenyl-5-pyrazolone. By LUDWIG KNORR (*Ber.*, 1895, **28**, 706—714; compare the foregoing abstract).—The technical pyrazolone (3 : 1-methylphenyl-5-pyrazolone) yields three isomeric series of substitution compounds, derived from the methylene-, imine- and phenol-form respectively. The derivatives of the phenol-form may be prepared by direct synthesis from the corresponding ethereal acetoacetate or from the technical pyrazolone by substitution. They are true pyrazole derivatives; their salts are dissociated by water, and they are reduced by alcohol and sodium to pyrazolines. Like the pyrazoles they are devoid of any antipyretic action on the organism. 5 : 3 : 1-Ethoxymethylphenylpyrazole has previously been prepared by Freer (Abstr., 1892, 953) and by Stolz (private communication).

It boils at 293—295°, and melts indefinitely at 40°. The *platinochloride* crystallises in characteristic groups of needles, and melts at 195°. When heated with hydrochloric acid at 160—170°, it is decomposed with formation of the technical pyrazolone and methylketole. On treatment with methylic iodide, followed by aqueous soda, the pyrazole is converted into antipyrine, whilst it is reduced by alcohol and sodium to 1 : 3-phenylmethylpyrazoline.

5 : 3 : 1-*Methoxymethylphenylpyrazole* may be obtained from methylic acetoacetate or by the methylation of technical pyrazolone. It boils at 247—248° (225 mm.), and forms a *platinochloride* which decomposes at 180—182°. 5 : 3 : 4 : 1-*Methoxydimethylphenylpyrazole* boils at 244—245° (225 mm.), and yields 3 : 4 : 1-dimethylphenylpyrazolone when treated with hydrochloric acid, whilst it is converted by methylic iodide into 4-methylantipyrine.

5-*Hydroxyethoxy*-3 : 1-*methylphenylpyrazole* is formed, along with the corresponding antipyrine, by the action of ethylenic chloride and sodium ethoxide on the technical pyrazolone (Aldrich, Dissert., Jena, 1892). It crystallises with 1 mol. H_2O, melts, when anhydrous, at 53—54°, and has the characteristic properties of its class. 4-*Bis*-5 : 2 : 1-*methoxymethylphenylpyrazole* is formed by the methylation of bismethylphenylpyrazolone, and melts at 186—187°. The condensation product of ethylic acetacetate with technical pyrazolone seems also to be a derivative of the phenol-form of pyrazolone.

The author proposes the term *double tautomerism* for cases in which three series of isomeric compounds are derived from a single parent substance.

Further details of the experimental work will shortly be published.

A. H.

The Aromatic Character of the Pyrazoles. By Ludwig Knorr (*Ber.*, 1895, **28**, 714—719).—The close analogy which has been pointed out between the derivatives of pyrazole and of benzene is strengthened by the following facts. Pyrazole is converted by fuming sulphuric acid into a sulphonic acid, melting at 330—335°. The mono-halogen derivatives behave in the same manner as the mono-halogen benzene derivatives, and 4-nitropyrazole is converted by reduction into a base which has all the characteristic properties of the aromatic bases, yields diazo-salts, and forms azo-colouring matters. At the same time, pyrazole possesses the properties of a weak secondary base. Thus, 1-methylpyrazole, which boils at 126—127°, is formed by heating silver pyrazole with methylic iodide. Pyrazole also yields a 1-*benzoylpyrazole*, boiling at 281°; a 1-*acetyl* derivative, boiling at 155—156°; a 1-*urethane*, boiling at 213°; and a 1-*carbamide*, melting at 136·5°. Full details of these compounds will be subsequently published.

4 : 1 : 3 : 5-Nitrotrimethylpyrazole (Abstr., 1894, i, 545) melts at 56—57° and boils at 245—247° (202 mm.). On reduction, it is converted into the *amido-compound*, which melts at 102—104°, is readily soluble in water and alcohol, and reduces silver oxide. The *hydrochloride* has the composition $C_6H_{11}N_3,2HCl$. It is converted by the action of nitrous acid into a diazo-salt, which at once yields azo-colouring matters with phenols, and also reacts with the technical

pyrazolone to form a *hydrazone of* 3 : 1-*methylphenyl*-4-*keto*-5-*pyrazolone*, $\begin{matrix}PhN-CO\\ \|\quad\ \\ N{:}CMe\end{matrix}>C{:}N{\cdot}NH{\cdot}C<\begin{matrix}CMe{\cdot}NMe\\ \|\quad\ \\ CMe{:}N\end{matrix}$, which crystallises in orange-coloured needles melting at 156°. The diazo-salt is very stable in aqueous solution, and only decomposes gradually when its solution is heated at 120°. A boiling solution of potassium iodide converts it into 4-*iodotrimethylpyrazole*, which melts at 75°. A. H.

1 : 3 : 5-Parethoxyphenylmethylethoxypyrazole. By FRIEDRICH STOLZ (*Ber.*, 1895, **28**, 635—639; compare Abstr., 1892, 1080).—When parethoxyphenylhydrazine is warmed with ethylic acetoacetate, 1 : 3 : 5-parethoxyphenylmethylpyrazolone is formed (*loc. cit.*). 1 : 3 : 5-*Parethoxyphenylmethylethoxypyrazole*,

$$N<\begin{matrix}N(C_6H_4{\cdot}OEt){\cdot}C{\cdot}OEt\\ \|\quad\quad\quad\ \|\\ CMe\text{———}CH\end{matrix},$$

is produced at the same time, and is obtained on evaporating the ethereal solution of the mixed bases after agitation with aqueous soda; it crystallises in yellowish prisms, and melts at 84°. It resists the action of boiling aqueous soda, hydrochloric acid, ferric chloride, and cupric acetate; the *hydrochloride* is decomposed by water. When heated with methylic iodide and methylic alcohol, it is converted into 1 : 2 : 3-parethoxydimethylpyrazolone (parethoxyantipyrine).

1 : 3 : 5-*Parahydroxyphenylmethylethoxypyrazole* is obtained by heating 1 : 3 : 5-parethoxyphenylmethylethoxypyrazole with concentrated hydrochloric acid for three hours at 150°; it crystallises in colourless plates, and melts at 195°. The substance dissolves in acids and alkalis, but is insoluble in alkali carbonates.

1 : 3 : 5-*Parahydroxyphenylmethylpyrazolone* is produced when the foregoing compound is heated with hydrochloric acid at 150° for two hours; it is also formed when 1 : 3 : 5-parethoxyphenylmethylpyrazolone is treated in the same manner. This substance melts at 230°, and dissolves in acids and alkalis; nitrous acid gives rise to a red *isonitroso*-derivative. When 1 : 3 : 5-phenylmethylpyrazolone is heated with hydrochloric acid for three hours, a small quantity of α-methylindole is formed, but the greater part of the pyrazolone derivative remains unchanged.

1 : 3 : 4 : 5-*Parethoxyphenylmethylnitroethoxypyrazole* is obtained by the action of nitrous acid on 1 : 3 : 5-parethoxyphenylmethylethoxypyrazole. It forms lustrous crystals, and melts at 119°.

M. O. F.

Phenometadiazine Derivatives. By AUGUST BISCHLER and H. P. MUNTENDAM (*Ber.*, 1895, **28**. 723—738; compare this vol., i, 250).—*Acetylparamethylisatic acid*, $NHAc{\cdot}C_6H_2Me{\cdot}CO{\cdot}COOH$, is prepared by the action of soda on acetylparamethylisatin, and melts at 166°.

β-Methylparatoluometadiazine-α-carboxylic acid,

$$C_6H_3Me<\begin{matrix}N=\!=\!=C\,Me\\ |\quad\quad\ |\\ C(COOH){:}N\end{matrix},$$

obtained by the action of alcoholic ammonia on the preceding compound, crystallises with $2H_2O$ in pale yellow plates, and melts at 160—161°, carbonic anhydride being evolved. The compound is readily soluble in water, mineral acids, glacial acetic acid, alkalis, and alkali carbonates. The *ammonium* salt crystallises in reddish needles and decomposes above 120°. The *silver salt* crystallises with $4H_2O$ in large, yellow, transparent prisms. The *mercurous*, *barium*, and *copper* salts are amorphous and sparingly soluble. The *methylic* salt crystallises in plates, the *ethylic* salt in large, yellow, flat prisms; they melt at 96° and 71° respectively. The *ethylic hydrochloride*, $C_{10}H_9N_2{\cdot}COOEt,HCl$, is sparingly soluble in ether. The *platinochloride* is reddish-yellow, the *picrate* yellow; both are sparingly soluble and pulverulent. The *amide*, $C_{10}H_9N_2{\cdot}CO{\cdot}NH_2$, is prepared by the action of alcoholic ammonia on the above ethylic salt or on acetylparamethylisatamide, it crystallises in long, colourless needles, and melts at 212°. Attempts to prepare the nitrile were unsuccessful.

β-Methylparatoluometadiazine, $C_6H_3Me{<}\begin{matrix}N{=}CMe\\ CH{:}N\end{matrix}$, is formed by heating the above ammonium salt with calcium oxide, but is most readily prepared by the distillation of the carboxylic acid; it crystallises in large, pale yellow plates, melts at 79°, and boils at 255° (726 mm.). The *hydrochloride* is pale yellow, pulverulent, and decomposes at about 180°. The *platinochloride* crystallises in orange-coloured, the *picrate* in golden, concentric needles; the latter melts at 145°.

α-Hydroxy-β-methylparatoluometadiazine, $C_6H_3Me{<}\begin{matrix}N{=}CMe\\ C(OH){:}N\end{matrix}$, is formed by the oxidation of the hydrocarbon with chromic anhydride, and has been previously prepared by Niementowski from orthamidoparatoluamide and acetic anhydride.

Propionylparamethylisatin, $C_6H_3Me{<}\begin{matrix}N(COEt)\\ CO\end{matrix}{>}CO$, formed from paramethylisatin and propionic anhydride, crystallises in golden plates, and melts at 143°. *Propionylparamethylisatic acid*,

$$COEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}CO{\cdot}COOH,$$

is prepared like the acetyl derivative, crystallises in small, colourless prisms, and melts at 161—162°.

β-Ethylparatoluometadiazine-α-carboxylic acid,

$$C_6H_3Me{<}\begin{matrix}N{=}CEt\\ C(COOH){:}N\end{matrix},$$

is obtained by the action of alcoholic ammonia on the preceding compound, and melts at 154°, carbonic anhydride being evolved. The *silver salt* crystallises in colourless plates; the *ammonium salt* is deposited in long, white, concentric needles, melting at 146°. Various sparingly soluble metallic salts have also been obtained. The *methylic salt* crystallises in small needles, and melts at 30°. The *ethylic salt*, which was not completely purified, was obtained as a pale yellow, oily liquid; it boils under reduced pressure without decompo-

sition. The *amide* crystallises in long, colourless needles, melts at 168°, and was prepared from *propionylparamethylisatic amide*, $COEt{\cdot}NH{\cdot}C_6H_3Me{\cdot}CO{\cdot}CONH_2$, which also crystallises in needles, and melts at 186°.

β-Ethylmetaparatoluodiazine, $C_6H_3Me<\begin{matrix}N=CEt\\ CH:N\end{matrix}$, is formed from the carboxylic acid or the ammonium salt, crystallises in yellow needles, melts at 38°, and boils at 265—266° (730 mm.). The *platinochloride*, $C_{11}H_{12}N_2,H_2PtCl_6$, is greyish-yellow.

The following phenyl derivatives were obtained in a similar manner to the preceding methyl and ethyl compounds.

Benzoylparamethylisatin, $C_6H_3Me<\begin{matrix}NBz\\ CO-\end{matrix}>CO$, crystallises in yellowish-green needles, and melts at 193°. *Benzoylparamethylisatic acid*, $NHBz{\cdot}C_6H_3Me{\cdot}CO{\cdot}COOH$, melts at 183°.

β-Phenylparatoluometadiazine-α-carboxylic acid,

$$C_6H_3Me<\begin{matrix}N=\!=\!=CPh\\ C(COOH):N\end{matrix},$$

is colourless, almost insoluble in water, and melts at 155°. The *silver salt* is pulverulent. The *ammonium salt* crystallises in colourless, silky, lustrous, concentric needles, and melts at 161°. The *ethylic salt* is deposited in prisms, and melts at 121°. The *amide* crystallises in concentric needles, which melt at 256°; it is prepared from *benzoylparamethylisatic amide*, $NHBz{\cdot}C_6H_3Me{\cdot}CO{\cdot}CONH_2$, which forms pale green needles melting at 219°.

β-Phenylparatoluometadiazine, $C_6H_3Me<\begin{matrix}N=CPh\\ CH:N\end{matrix}$, obtained from the carboxylic acid, crystallises in small, straw-coloured plates, melts at 133°, boils above 360°, and has no smell. The *hydroxyl-derivative* is yellow and sparingly soluble. J. B. T.

Imidazolones and their Decomposition Products. By Hans Rupe (*Ber.*, 1895, **28**, 777—780).—Amidocamphorcarbamide,

$$C_8H_{14}<\begin{matrix}CO\\ CH{\cdot}NH{\cdot}CO{\cdot}NH_2\end{matrix},$$

(Abstr., 1894, i, 241), when heated with zinc chloride or with strong sulphuric acid, yields *camphorimidazolone*, $C_8H_{14}<\begin{matrix}C{\cdot}NH\\ \|\\ C{\cdot}NH\end{matrix}>CO$, or perhaps $C_8H_{14}<\begin{matrix}C=\!=N\\ CH{\cdot}NH\end{matrix}>CO$. This crystallises in tiny, white needles, and melts above 320°; it resembles phenylimidazolone (Abstr., 1894, i, 241; this vol., i, 218) in its properties. It does react with acetic anhydride in the presence of sodium acetate, but the product is not a simple acetyl derivative. C. F. B.

Dithiourazole and its Derivatives. By Martin Freund and Hans Imgart (*Ber.*, 1895, **28**, 946—957; compare Abstr., 1894, i, 97

and 477).—Dithiourazole, $NH<\begin{matrix}CS\cdot NH\\ |\\ CS\cdot NH\end{matrix}$, is obtained by the action of boiling hydrochloric acid on hydrazodicarbonthiamide (*loc. cit.*), which loses 1 mol. of hydrogen sulphide under these conditions. It crystallises from water and dilute alcohol in colourless, rhombic prisms; it sinters at 240° and melts at 245°. The *acetyl* derivative crystallises from water in plates; at 250° it becomes brown, and melts at 300°, undergoing decomposition. It dissolves in dilute alkalis, and is precipitated from solution on the addition of acids. The *azo*-compound, $C_2HN_3S_2$, is formed on oxidising dithiourazole with ferric chloride or hydrogen peroxide; it crystallises in slender, yellow plates, and melts at 244—245°. On acidifying the alkaline solution of this substance, dithiourazole is regenerated.

Imidothiourazole, $NH<\begin{matrix}CS——NH\\ |\\ C(NH)\cdot NH\end{matrix}$, is also formed when hydrazodicarbonthiamide is heated with hydrochloric acid, and, owing to its basic properties, can easily be separated from dithiourazole. It crystallises from ether in colourless prisms, which sinter at 215° and melt at 221—223° (compare *loc. cit.*). The *hydrochloride* forms colourless crystals, which contain $1H_2O$. The *diacetyl* derivative crystallises from hot water in slender, white needles; it becomes brown at 291°, and does not melt below 315°. It resists the action of acids and alkalis, and is scarcely soluble in cold water or alcohol.

Hydrazodicarbonthioethylamide, $N_2H_2(CS\cdot NHEt)_2$, is prepared by heating hydrazine sulphate (1 mol.) and the calculated quantity of sodium carbonate with ethylthiocarbimide (2 mols.) dissolved in alcohol; it crystallises in lustrous, colourless leaflets, sinters at 190°, and decomposes at 270°. It undergoes no change when dissolved in cold concentrated sulphuric acid.

Ethyldithiourazole, $NEt<\begin{matrix}CS\cdot NH\\ |\\ CS\cdot NH\end{matrix}$, is obtained from the foregoing substance by the action of boiling hydrochloric acid. It crystallises from water in aggregates of colourless prisms, and melts at 140°. The *sodium* salt forms colourless prisms; it dissolves in alcohol, and melts at 170°. The *silver* salt is colourless, and becomes black when heated. Ethyldithiourazole is not desulphurised when an aqueous solution of the sodium salt is heated with mercuric oxide, and no silver sulphide is formed when the ammonium salt is heated with ammoniacal silver solution. The *nitroso*-compound is obtained on adding concentrated nitric acid to the hot, aqueous solution; it is also formed when dilute hydrochloric acid is added to the mixed solutions of sodium nitrite and the sodium salt of ethyldithiourazole. The compound crystallises from alcohol in pale yellow needles, and melts at 118—120°; it gives Liebermann's reaction. The *azo*-compound, $C_4H_5N_3S_2$, is formed on adding a concentrated solution of potassium nitrite to the hot, aqueous solution of ethyldithiourazole. It crystallises in yellow plates, and melts at 198°; when treated with alcoholic ammonium sulphide, it yields the original substance. On adding a freshly-prepared solution of diazobenzene chloride to an ice-cold solution of ethyldithiourazole in excess of sodium carbonate, a

yellow substance is precipitated, which soon becomes greyish-brown; while in a moist condition it explodes when spread on a porous tile.

Methylethyldithiourazole is obtained by heating an alcoholic solution of ethyldithiourazole with sodium ethoxide (1 mol.) and methylic iodide (1 mol.) for two hours; it crystallises in colourless leaflets, and melts at 88°.

Ethylimidoethylthiourazole, $NEt<\begin{matrix}CS\text{---}NH\\ |\quad\quad|\\ C(NEt)\cdot NH\end{matrix}$, is formed, together with ethyldithiourazole, when hydrazodicarbonthioethylamide is treated with boiling hydrochloric acid. It crystallises from water in colourless prisms, and melts at 173°. The *hydrochloride* contains $1H_2O$, and melts at 98°. The *nitroso*-derivative crystallises from alcohol in lustrous, golden leaflets, sinters at 135°, and melts at 145°. The *diacetyl* derivative forms white needles, and melts at 165°. When ethylimidoethylthiourazole is heated with methylic iodide at 100°, the *hydriodide* of a monomethylated base is formed; it crystallises from alcohol in white needles, and melts at 181°.

Phenyldithiourazole, $NPh<\begin{matrix}CS\cdot NH\\ |\quad\quad|\\ CS\cdot NH\end{matrix}$, is obtained by the action of hydrochloric acid on hydrazodicarbonthiophenylamide. It crystallises in colourless leaflets, sinters at 205°, and melts at 219°. The *azo*-compound, $C_8H_5C_3S_2$, forms reddish-yellow plates, sinters at 230°, and melts at 240°. The *acetyl* derivative crystallises in lustrous, white leaflets, sinters at 240°, and melts at 252°. When treated with hydrogen peroxide or nitrous acid, the alcoholic solution yields a *compound*, $C_{12}H_{16}N_6S_4O_2$, which has the properties of a bisulphide. It sinters at 195° and melts at 208°; on reduction with zinc and hydrochloric acid, the acetyl derivative is regenerated. The *diacetyl* derivative crystallises from alcohol in slender, yellow needles; it sinters at 168° and melts at 176°. M. O. F.

Thebaïne. By Martin Freund and Ernst Göbel (*Ber.*, 1895, **28**, 941—944; compare this vol., i., 117).—When thebaïne is heated during several hours with acetic anhydride, it yields methylhydroxyethylamine and the *acetyl* derivative of thebaol, which melts at 118—122° and is insoluble in alkalis. *Thebaol*, $C_{14}H_7(OMe)_2\cdot OH$, is obtained from the acetyl derivative; it melts at 94°. Acetylthebaol is also formed when thebaïne methiodide is treated with boiling acetic anhydride in presence of silver acetate, dimethylhydroxyethylamine being produced at the same time; on oxidation with chromic anhydride and glacial acetic acid, it yields *acetylthebaolquinone*, which crystallises in yellow needles and melts at 203°. *Thebaolquinone*, $C_{14}H_6O_2(OMe)_2\cdot OH$, forms brown leaflets and melts at 233°; it condenses with tolylenediamine forming the phenanthrazine *derivative*, $OH\cdot C_{14}H_5(OMe)_2\ll\begin{matrix}N\\ N\end{matrix}>C_6H_3Me$, which melts at 192°, whilst the *compound* derived from acetylthebaolquinone crystallises in yellow needles and melts at 201—203°.

These observations confirm the view already put forward regarding the constitution of thebaïne (*loc. cit.*), which is derived from a

dihydrophenanthrene, whilst morphine and codeïne, to which thebaïne is closely related, are tetrahydrophenanthrene derivatives.

M. O. F.

Brucine Hydropolysulphide. By OSCAR G. DOEBNER (*Arch. Pharm.*, 1994, **232**, 693—697).—When an alcoholic solution of brucine is treated with a solution of sulphur in alcoholic ammonium sulphide, a *hydropolysulphide*, $(C_{23}H_{26}N_2O_4)_2H_2S_8 + 2H_2O$, is formed. The orange-red crystals are insoluble in water, alcohol, ether, benzene, and carbon bisulphide. The hydropolysulphide retains the characteristic physiological properties of brucine, although in a lessened degree. This compound appears to be different from the brucine polysulphide obtained by E. Schmidt, which probably contained 6 atoms of sulphur, and was analogous to the strychnine hexasulphide first prepared by Hofmann.

L. T. T.

Cinchotenine. By FLORIAN RATZ (*Monatsh.*, 1894, **15**, 787—802; compare Skraup, *Annalen*, **197**).—The *ethyl derivative* of cinchotenine, $C_{18}H_{19}EtN_2O_3$, obtained on treating the alkaloïd with ethylic iodide and sodium ethoxide, melts at 210·5°, and gives the following derivatives:—A *hydrochloride*, $C_{18}H_{19}EtN_2O_3.2HCl$, which decomposes at 231—232°; a *platinochloride*, $C_{18}H_{19}EtN_2O_3,H_2PtCl_6$, which decomposes at 200°; an *ethiodide*, $C_{18}H_{19}EtN_2O_3,EtI$, crystallising in pale yellow needles, which melt and decompose at 212—213°; and a *sesquiethiodide*, $[C_{18}H_{19}EtN_2O_3]_2.3EtI$, which crystallises in bright yellow needles, melts and decomposes at 183°, and when treated with hot water is converted into a mixture of the *monethiodide* described above and a *diethiodide*, $C_{18}H_{19}EtN_2O_3,2EtI + H_2O$. The latter crystallises in deep yellow prisms, and melts at 154°. Ethylcinchotenine does not appear to change when treated with nitrous acid.

With acetic chloride, cinchotenine yields the compound

$$C_{18}H_{19}AcN_2O_3,2HCl,$$

a pale yellow, crystalline powder, which is insoluble in ether and melts and decomposes at 183—184°. With benzoic chloride, cinchotenine forms an amorphous, yellow powder, $C_{18}H_{19}BzN_2O_3.HCl + H_2O$, which melts and decomposes at 197°, and does not form an additive compound with hydriodic acid, so that the double linking existing in cinchonine appears to be broken through during the oxidation to cinchotenine.

G. T. M.

Cinchotenine. By PAUL FORTNER (*Monatsh.*, 1895, **16**, 62—67).—When cinchotenine and phosphorus pentachloride are mixed with phosphorus oxychloride, and heated for some hours at 100°, a product is obtained which is probably an acid chloride, since, on treatment with water and alcohol, it yields cinchotenine and ethylcinchotenine respectively. This behaviour, taken in conjunction with the facts that cinchotenine readily undergoes ethylation, and that it dissolves in cold, dilute alkaline solutions, points to the presence of a carboxyl group in the alkaloïd.

G. T. M.

Action of Hydriodic acid on Cinchotine and on Hydroquinine. By GUSTAV PUM (*Monatsh.*, 1895, **16**, 68—74).—*Cinchotine*

dihydriodide, $C_{19}H_{24}N_2O,2HI$, forms anhydrous, yellow crystals, which darken at 232°, and melt and decompose at 263—264°. It remains unchanged when heated for five hours at 100° with hydriodic acid.

Hydroquinine dihydriodide, $C_{20}H_{26}N_2O_2,2HI$, separates from a solution in 50 per cent. alcohol in bright yellow crystals containing $3H_2O$. On heating with hydriodic acid at 100°, the salt $C_{19}H_{24}N_2O_2,2HI$ is obtained. It forms yellow crystals, which turn brown at 228° and melt and decompose at 239—240°. The corresponding base, obtained by the addition of sodium carbonate to the hydriodide, darkens at 165°, melts at 170°, and, unlike hydroquinine, is readily and perfectly soluble in aqueous potash. It is noteworthy that cinchotine and hydroquinine have not the same power to take up hydrogen iodide as is possessed by cinchonine and quinine, each of which contains 2 atoms of hydrogen less than the bases first named.

G. T. M.

Cinchonigine. By Émile Jungfleisch and Eugène Léger (*Compt. rend.*, 1895, **120**, 325—328).—Cinchonigine (Abstr., 1888, 308, 507, 612) is dimorphous, and with the exception of strontium hydrogen tartrate, which does not exist in solution, it is the first example of a dimorphous compound with a specific rotatory power.

When a carefully dried ethereal solution of cinchonigine is allowed to crystallise at the ordinary temperature, the crystals are monoclinic, but, if crystallisation takes place in the hot solution, the crystals belong to the rhombic system. Different portions of the same solution will yield the two different kinds of crystals according to the temperature of crystallisation, and the tendency to form one or the other is increased by the introduction of ready-formed crystals. Further, if a monoclinic crystal is added to the rhombic crystals in ether at a low temperature, they are gradually and completely transformed into monoclinic crystals. On the other hand, if the monoclinic crystals, moistened with ether saturated with cinchonigine, are mixed with a rhombic crystal and heated in a sealed tube at 45—50° for some hours, the whole mass changes to rhombic crystals. Both crystals melt at the same temperature, and when converted into the hydrochloride have the same rotatory power; their salts and other derivatives are also identical.

Cinchonigine, which when dry melts at 129°, melts in boiling water, and the liquid on cooling deposits crystals of a hydrate, which is best obtained by saturating ether with both water and cinchonigine and allowing it to evaporate slowly. The crystals are rhombic and hemihedral; they contain $2H_2O$, melt at 69·3° (corr.), and are stable in ordinary air, but lose their water in dry air or at 100°. The closely related cinchoniline forms a hydrate with $3H_2O$.

C. H. B.

Organic Chemistry.

Action of Magnesium on the Vapours of the Alcohols. Preparation of Allylene. By EDWARD H. KEISER and MARY B. BREED (*Chem. News*, 1895 **71**, 118—120).—Magnesium glows when heated in a current of the vapour of methylic, ethylic, or propylic alcohol; a large volume of gas is at the same time given off, and a black, coherent mass remains, which, on treatment with water and a small quantity of ammonium chloride, evolves a moderately rapid current of allylene. The gas evolved during the glowing of the magnesium had the following percentage composition.

	With methylic alcohol.	With ethylic alcohol.	With propylic alcohol.
CO_2	0·8	0·0	0·0
CO	0·6	0·4	3·5
CH_4 or saturated hydrocarbons	19·7	11·1	19·9
C_2H_2 or unsaturated hydrocarbons	—	10·0	17·8
C_3H_4 or unsaturated hydrocarbons	—	4·0	
H	78·9	72·9	57·8

The decomposition of the same alcohols by passing the vapour over heated iron, yielded gases of the following percentage composition.

	Methylic alcohol.	Ethylic alcohol.	Propylic alcohol.
CO_2	3·8	0·5	0·6
CO	26·8	8·0	16·4
Saturated hydrocarbons	1·6	13·0	23·6
Unsaturated hydrocarbons	—	4·0	16·7
Hydrogen	67·4	63·8	42·7

In the case of the magnesium, the carbonic oxide is reduced. Allylic, isobutylic, and amylic alcohols were found to behave in a similar manner; a small quantity of acetylide was found in the black residue in the case of propylic alcohol. The production of allylene from propylic and allylic alcohols, in the manner described, proceeds with such facility that it is recommended as a method of preparing allylene. D. A. L.

Crystalline Copper-ferrocyanides. By J. MESSNER (*Zeit. anorg. Chem.*, **8**, 368—393).—When potassium ferrous ferrocyanide, $K_2Fe(FeC_6N_6)$, is treated with ferric salts and water, a violet amorphous precipitate is obtained, containing from 6 to 12 per cent. of potassium, according to the temperature at which the action takes place. If a cupric salt is employed in place of the ferric salt, then a beautiful, violet compound is obtained, which, like the iron compound, is converted by oxidation into a green powder. This violet com-

pound, which probably has the composition $K_2CuFe_2(FeC_6N_6)_2$, is slowly and incompletely decomposed by boiling with alkali carbonates or hydroxides, and the solution so obtained contains copper, which can be precipitated by hydrogen sulphide. If the violet compound is decomposed by potassium carbonate, the solution, on cooling, deposits crystals of the compound obtained by boiling copper ferrocyanide with potassium ferrocyanide; this compound cannot, however, be obtained pure. When sodium carbonate is employed in place of potassium carbonate, the compound $Na_2Cu(FeC_6N_6)$ is obtained in beautiful, brown, quadratic prisms.

Sodium cuproferrocyanide, $Na_2Cu_2(FeC_6N_6)$, is obtained by adding a cold saturated solution of the double cyanide of copper and sodium to a hot solution of sodium ferrocyanide. It crystallises from the solution, on cooling, in colourless, microcrystalline, six-sided prisms, and may be dried in a vacuum over sulphuric acid. It is also obtained by boiling a solution of sodium ferrocyanide with cuprous cyanide, and, after adding a small quantity of neutral sodium sulphite, cooling the solution in a current of hydrogen. The compound contains 27·5 per cent. of water. When exposed to the air, it slowly oxidises and turns brown. When heated at 100°, it turns brown and loses part of its water of crystallisation, but the whole of the water of crystallisation can only be removed by ignition. At 200°, it glows and decomposes, and at 180°, it is converted into a brown powder which still contains water. It is insoluble in water, alcohol, and ether, dissolves in alkali cyanides with decomposition, and is decomposed by acids and alkalis.

Sodium cupriferrocyanide, $Na_2Cu(FeC_6N_6)$, is formed when cupric salts are boiled with a solution of sodium ferrocyanide. It is most easily prepared by boiling copper ferrocyanide, prepared from copper sulphate and hydroferrocyanic acid, with sodium ferrocyanide, and, after filtering off the amorphous precipitate, allowing the filtrate to evaporate exposed to the air. Or it can be obtained by passing a current of air through the hot mother liquors of the cuprous salt and then allowing the oxidised compound to crystallise. It crystallises in lustrous, brown, four-sided prisms, is insoluble in cold water, and decomposes when boiled with water or with dilute acids or alkalis. It dissolves in potassium cyanide with evolution of cyanogen, and yields potassium cuprous cyanide and potassium ferrocyanide. When copper ferrocyanide is boiled with a solution of sodium ferrocyanide, a bright green compound is produced, which is converted into the brown compound after one to two hours' boiling; this phenomenon does not take place in the case of the potassium salts. The author was unable to determine whether the green substance is a definite compound, as it is very easily decomposed. The mother liquors of sodium cupriferrocyanide and sodium cuproferrocyanide, when mixed with dilute acids, yield white, amorphous precipitates, which are probably the acids $H_2Cu(FeC_6N_6)$ and $H_2Cu_2(FeC_6N_6)$. When freshly prepared, they dissolve in alkali carbonates and hydroxides, and quickly decompose to yield ferrocyanic acid.

Potassium cuproferrocyanide, $K_2Cu_2(FeC_6N_6)$, is obtained in like manner to the sodium salt by boiling copper cyanide with a solution

of potassium ferrocyanide containing a small quantity of potassium sulphite, or by boiling potassium cuprous cyanide or cuprous chloride with potassium ferrocyanide. It crystallises in colourless cubes if the solution is quickly cooled. When the solution is slowly cooled, it is obtained mixed with partially oxidised crystals of a yellow to brown colour. It contains 18·7 to 20·4 per cent. of water, and closely resembles the sodium salt.

The author was unable to obtain potassium cupriferrocyanide in a pure state, as under all conditions the cupro-salt is formed at the same time.

Ammonium cuproferrocyanide is obtained by boiling copper cyanide with a solution of ammonium ferrocyanide containing ammonium sulphite and passing hydrogen through the mixture. It crystallises in small, colourless, six-sided prisms, decomposes rapidly under water, or on exposure to air, or in a vacuum, with formation of hydroferrocyanic acid, and is at once decomposed by acids and alkalis. It can also be obtained by treating a solution of the sodium salt with ammonium nitrate.

Ammonium cupriferrocyanide is obtained by boiling copper ferrocyanide with a solution of ammonium ferrocyanide. The solution thus obtained must be filtered as quickly and as hot as possible. It crystallises in brownish-red cubes, can be dried in a vacuum over sulphuric acid, and has properties similar to those of the sodium salt.

Magnesium cuproferrocyanide is obtained by boiling copper cyanide with a solution of magnesium ferrocyanide. It crystallises in beautiful, colourless, six-sided prisms, turns brown on exposure to air and in a vacuum over sulphuric acid, and is less stable than the analogous sodium and potassium salts.

Magnesium cupriferrocyanide is easily obtained by boiling copper ferrocyanide with magnesium ferrocyanide. It separates in violet-brown crystals and contains 44·3 to 44·5 per cent. of water.

Calcium cupriferrocyanide crystallises in small, brown, quadratic prisms, and can be dried in a vacuum over sulphuric acid.

Strontium cupriferrocyanide and *barium cupriferrocyanide* are obtained in crystals having the same form and colour as the calcium salt.

Calcium, *strontium*, and *barium cuproferrocyanides* are obtained by boiling copper cyanide with the corresponding ferrocyanides. They crystallise in colourless, six-sided prisms, which cannot be distinguished from one another, but the pure compounds cannot be obtained as the simple ferrocyanide always separates with them, and an excess of ferrocyanide is necessary in their preparation, as the cuproferrocyanides are not soluble in water except in the presence of an excess of ferrocyanide.

Copper ferrocyanide ammonia, $Cu_2(FeC_6N_6),8NH_3$, is obtained by adding a solution of ammonium ferrocyanide in strong ammonia to a solution of cuprous chloride in the strongest ammonia, and allowing the mixture to remain for a few hours. It crystallises in beautiful, black, lustrous prisms, is very sparingly soluble in ammonia, and is not decomposed by cold absolute alcohol. The crystals, on exposure to air, quickly decompose into ammonia, copper ferrocyanide, and the compound $Cu_2(FeC_6N_6),4NH_3$. With dilute acids, it yields copper

ferrocyanide and ammonium salts. When evaporated on the water bath in its own mother liquor, it is converted into ammonium cupriferrocyanide and amorphous compounds. E. C. R.

A New Alcohol from Lanolin. By G. MARCHETTI (*Gazzetta*, 1895, **25**, i, 42—49).—After hydrolysing lanolin by heating it on the water bath with alcoholic sodium ethoxide, distilling off the solvent, acidifying with sulphuric acid, and extracting the cholesterols, alcohols, and aliphatic acids with ether, a residue of *lanolinic alcohol*, $C_{12}H_{24}O$, remains; on purification with alcohol and chloroform, it is obtained as a white, odourless powder, or as spheroidal concretions, melting at 102—104°. It is soluble in hot alcohol, chloroform, or benzene, but insoluble in potash or ether; it is precipitated unchanged by acids from its solution in sodium ethoxide, and is not acted on by iodine or acetic anhydride. The *benzoate*, $C_{12}H_{23}OBz$, forms a white, waxy mass, melting at 65—66°, which decomposes on exposure to the air, and is hydrolysed by sodium ethoxide.

Lanolinic acid, $C_{12}H_{22}O_3$, is prepared by oxidising lanolinic alcohol with chromic acid in acetic acid solution; it is a white, crystalline powder, melting at 75—77°, and is soluble in alcohol, ether, chloroform, benzene, or alkali carbonates, but is insoluble in water. Its *barium* salt, $(C_{12}H_{21}O_3)_2Ba$, crystallises with $1H_2O$ which is lost at 150°, and decomposes when heated. W. J. P.

The Polymerides of Epichlorhydrin. By EMANUELE PATERNÒ (*Gazzetta*, 1894, **24**, ii, 541—544).—The author supplements Oliveri and Paternò's cryoscopic examination of the polymeride of epichlorhydrin (Abstr., 1894, i, 486) by new determinations in benzene and acetic acid, and by boiling point determinations in benzene; the results of these experiments indicate that the substance probably has the molecular composition $(C_3H_5ClO)_5$. The behaviour in freezing benzene shows that the compound has marked alcoholic properties; on treatment with cold alcoholic potash, it yields an oil, which boils at 250—300° with slight decomposition, and yields about 53 per cent. of ethoxyl by Zeisel's method; it possibly has the composition $C_{12}H_{20}(OEt)_4O_4$. W. J. P.

Amorphous Condition of Fused Substances. By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 630—632).—The glucose pentacetins (this vol., i, 321) crystallise in needles, whilst the hexacetins of racemo-inosite and the active inosites form hard and somewhat bulky crystals. If, however, they are melted in narrow tubes and allowed to cool, they all solidify in amorphous forms, which melt at 40—50° below the normal melting points. When the amorphous forms are melted, they gradually change into the crystalline forms with normal melting points, the change being more rapid the smaller the difference between the melting points of the crystallised and amorphous forms. The change from amorphous to crystalline is accompanied by development of heat, and is strictly analogous to the conversion of plastic sulphur into the crystalline form. It would follow that there is no essential difference between the allo-

tropic modifications of the element and the crystallised and amorphous forms of the compounds in question.

Many other carbon compounds behave like the acetins and solidify in an amorphous form when melted and suddenly cooled. When heated, however, the amorphous forms become crystalline with development of heat, the change being very rapid in some cases and gradual in others. C. H. B.

Combination of Sugars with Primary Hydrazines: Amidoguanidine, and Arabinose. By R. RADENHAUSEN (*Chem. Centr.*, 1894, ii, 776; from *Zeit. Ver. Rübenzuck.-Ind.*, 1894, 768—770; compare H. Wolff, Abstr., 1894, i, 315).—Amidoguanidine reacts with arabinose in alcoholic solution, a condensation with the aldehyde group occurring with separation of water; the product crystallises in small, white needles, melts at 125° (uncorr.), and dissolves in water and in alcohol, but not in ether.

The reaction between hydrazine hydrate and arabinose gives rise to a deep-seated decomposition of the sugar, and no crystalline product has been isolated. Nitrobenzoylhydrazine and arabinose, however, form a condensation product, which crystallises in snow-white tablets, and melts at 178°; it is insoluble in cold water, and is decomposed into the parent substances when heated with water—a behaviour which is remarkable, since all compounds of hydrazines with aldehydes which have been prepared heretofore are stable in hot water. A. G. B.

A Second Achroodextrin obtained by the Action of Diastase on Starch. By CARL J. LINTNER and GEORG DÜLL (*Chem. Centr.*, 1894, ii, 864; *Zeit. ges. Brauw.*, 1894, **17**, 339—340).—The new dextrin, hitherto overlooked because it forms only a small proportion of the products of conversion, has the formula $(C_{12}H_{20}O_{10})_3 + H_2O$. The opticity is $[\alpha]_D = 183°$, and the cupric reduction R = 26·5—26·8. No evidence of a third achroodextrin, $(C_{12}H_{20}O_{10})_2 + H_2O$, has been obtained. This new achroodextrin II has the same composition as that of the substance described by Brown and Morris as typical maltodextrin, but the opticity and cupric reduction given for this substance leave no doubt that it is not pure, but contains both achroodextrin I and isomaltose. A. G. B.

Wax Found in the Treatment of Cotton and Linen Fibre for the Manufacture of Paper. By CLAYTON BEADLE (*Chem. News*, 1895, **71**, 164—165).—Occasionally when disintegrating fibre that has been treated under pressure with $3\frac{1}{2}$ per cent. caustic soda and bleached with calcium hypochlorite at 32°, a deposit forms on surfaces in the beater. This consists of aluminium, iron, and calcium salts mixed with a sweet-smelling waxy substance, soluble in ether, melting at 47·5°, having a saponification equivalent of 19·46 (KHO), and yielding 91·04 per cent. of insoluble fat acids. It is not noticed in the raw fibre. D. A. L.

Derivatives of Active α-Hydroxybutyric acid. By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1895, **120**, 632—635).—

The ethereal salts of the lævogyrate α-hydroxybutyric acid (this vol., i, 333) were prepared in the usual way; their physical properties are as follows, the alkylic radicles being primary in all cases.

	Boiling point.	Sp. gr. at 15°.	Specific rotatory power $[\alpha]_D$.	Product of asymmetry $P \times 10^6$.
Ethylic salt	169°	0·978	−1·9	319
Normal butylic salt..	200	0·982	−9·7	309
Isobutylic salt.....	197	0·965	−7·7	309
Racemic amylic salt..	209	0·950	−8·5	286
Heptylic salt.....	245	0·928	−6·1	233
Octylic ,, ...	255	0·916	−5·3	209

The maximum of P corresponds with the propylic salt, the value being 330. The rotatory power also passes through a maximum, but the two maxima do not coincide.

The results obtained with the various amylic salts are as follows.

	$[\alpha]_D$.
1. Racemic hydroxybutyric acid and active alcohol	+1·5
2. Lævogyrate hydroxybutyric acid and racemic alcohol.	−8·5
3. ,, ,, ,, and lævogyrate alcohol.....	−7·3
4. Dextrogyrate ,, ,, and lævogyrate alcohol	+8·1

These results afford further proof of the superposition of the effects of different asymmetrical carbon atoms in the same molecule. The calculated rotatory power of ethereal salt No. 3 is −7·0, and the observed value −7·3; in the case of No. 4 the calculated and observed values are +7·8 and +8·1 respectively (compare this vol., ii, 149 and 195). C. H. B.

Condensation of Ketones with Ethylic Salts of Dibasic Acids under the Influence of Sodium Ethoxide. By Hans Stobbe (*Ber.*, 1895, **28**, 1122—1123).—In consequence of the publications of Japp and Davidson (Trans., 1895, 132) and Meyenberg (this vol., i, 334), the author states that he is extending his research (Abstr., 1894, i, 594), and examining the condensation of various ketones and diketones with ethylic succinate, pyrotartrate and malonate, and of the last with ethylic acetoacetate. From acetone and ethylic malonate, two acids have already been obtained melting at 74—76° and at 146—148°. C. F. B.

Condensation of Ethylic Malonate with Acetone. By Karl Auwers (*Ber.*, 1895, 1130—1133).—In an attempt to synthesise norcamphoric acid, now given up on account of Meyenberg's paper (this vol., i, 334), ethylic dimethylacrylate, $CMe_2{:}CH{\cdot}COOEt$, was condensed by heating it with ethylic potassiomalonate and a little alcohol at 98°, and a compound, $CH(COOEt)_2{\cdot}CMe_2{\cdot}CHK{\cdot}COOEt$, was obtained; the ethylic salt, after the potassium is replaced by hydrogen, boils at 194° under 43 mm. pressure, and has sp. gr. = 1·064 at

13·5°. When hydrolysed with rather strong acids, it yields *ββ-dimethylglutaric acid*, $CMe_2(CH_2{\cdot}COOH)_2$; this melts at 100—101°, and, when treated with acetic chloride or distilled under atmospheric pressure, yields an *anhydride* melting at 124°.

β-Bromisovaleric acid was prepared by treating dimethylacrylic acid with hydrobromic acid saturated at 0°; it melts at 73·5°.

C. F. B.

Conversion of Carbamide into Cyanamide. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1894, [3], **11**, 1068—1070; compare Fenton, Trans., 1882, 262).—Carbamide is readily and energetically dehydrated by sulphurous chloride, abundance of sulphurous anhydride and hydrogen chloride being evolved when the two are mixed. After the excess of the reagent has been removed by means of sodium carbonate solution, the cyanamide is extracted from the product with ether.

JN. W.

Mercuric Compound of Thiophen: Estimation of Thiophen in Benzene. By GEORGES DENIGÈS (*Compt. rend.*, 1895, **120**, 628—630).—The compounds of mercury with thiophen hitherto known are formed from the chloride under special conditions, but the author finds that thiophen combines readily with mercuric sulphate in acid solution, and also with mercuric acetate and chloride under similar conditions. The reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. If 200 c.c. of this liquid is mixed with 1 c.c. of thiophen, it rapidly becomes turbid at the ordinary temperature, but the liquid should be first gently heated, and finally boiled.

A basic *mercuriothiophen sulphate*, $(HgSO_4,HgO)_2C_4SH_4 + H_2O$, separates as a heavy, coherent, white, precipitate, formed of radiating spheroids, and is washed with boiling water and dried. It loses 1 mol. H_2O at 100—110°, and may be heated for a long time at 120—130°, or even at 150°, without undergoing any further change. Above 200°, sulphurous anhydride and thiophen are given off. It is insoluble in water and neutral solvents, but dissolves in acids, with gradual liberation of thiophen, as indicated by the isatin and alloxan or alloxantin reactions, the change being accelerated by heat. Hydrogen sulphide or alkali sulphides precipitate the mercury and liberate thiophen, but ammonia and caustic alkalis have no action even on heating.

The ease with which this compound is formed, and its insolubility, affords a valuable means of detecting and estimating thiophen in commercial benzene.

C. H. B.

Hexamethylene. By NICOLAI D. ZELINSKY (*Ber.*, 1895, **28**, 1022—1025).—Hexamethylene, prepared by reducing iodohexamethylene (Baeyer, Abstr., 1894, i, 174) in alcoholic solution with zinc and hydrochloric acid, boils at 81—82°, has the sp. gr. 0·7764 at 20°/4°, and the refractive index 1·4258. Hexahydrobenzene, prepared by the direct reduction of benzene with hydriodic acid (Kishner, *J. Russ. Chem. Soc.*, 1894, 375), on the other hand, boils at 72—73°, has the sp. gr. 0·7488, and the refractive index 1·4101, so that the two com-

pounds seem to be distinct. The hydrocarbon, prepared by the reduction of iodohexamethylene with hydriodic acid at 220°, has properties which are intermediate between those of the two substances just described, and probably contains both of them.

A. H.

The Use of Metallic Aluminium in the Synthesis of Aromatic Hydrocarbons. By CORNELIUS RADZIEWANOWSKI (*Ber.*, 1895, **28**, 1135—1140).—Instead of aluminium chloride, aluminium itself, together with either hydrochloric acid or mercuric chloride, may be used to effect the Friedel-Crafts synthesis. A small quantity of aluminium shavings is placed in excess of benzene, gaseous hydrogen chloride passed in for 20 minutes, and the mixture allowed to remain until the metal turns brown and a copious evolution of hydrogen begins; the chloride or bromide of the other radicle is then added drop by drop, the mixture being cooled with water, or the chloride or bromide is added drop by drop to a mixture of aluminium shavings and mercuric chloride with excess of benzene, the mixture being cooled with ice. Diphenylmethane and ethylbenzene were prepared by both methods from benzylic chloride and ethylic bromide respectively; isopropylbenzene, from isopropylic chloride, by the first method only. This method does not bring about the condensation with chloroform to triphenylmethane, nor with benzylic chloride to anthracene. The second method will effect the first of these condensations, but not the second. The yield was usually 60—70 per cent. of the theoretical.

C. F. B.

Argon in Combination. By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, **120**, 581—584).—When argon is mixed with benzene vapour and subjected repeatedly to the action of the silent electrical discharge, the benzene being renewed from time to time, condensation takes place and a product is formed similar to that obtained from benzene and nitrogen under similar conditions; it is a yellow resinous odorous substance which when heated yields alkaline vapours and an abundant carbonaceous residue.

If the molecular weight of argon were 42, it would stand in this respect in the same relation to nitrogen as ozone does to oxygen.

C. H. B.

Ethylquinone. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], **11**, 1130—1131).—*Ethylquinone*, prepared from dimethylanilethylquinonimide (this vol., i, 417), crystallises in brilliant, golden-yellow plates, or long, prismatic needles. It has a powerful odour, and its vapour irritates the eyes and nose. It melts at 38·2°, and is readily volatile at ordinary temperatures. The corresponding *quinol*,

$$C_6H_3Et(OH)_2 \ [(OH)_2 : Et = 1 : 4 : 2],$$

prepared by reducing the quinone with sodium hydrogen sulphite, crystallises in colourless plates or prismatic needles, and melts at 112—113°; it sublimes easily. The solution in alkalis soon becomes coloured.

JN. W.

Purification of Guaiacol by strongly Cooling it. By LUDWIG WENGHÖFFER (*Chem. Centr.*, 1894, ii, 565; from *Pharm. Zeit.*, 1894, **39**, 576—577).—Liquid guaiacol is kept for a day at a temperature of −100° and then separated, by a peculiar artifice, into two layers; the larger and clearer of these is "Riedel-Pictet guaiacol," the other is a brownish-yellow residue. Riedel's guaiacol has a sp. gr. at 24° of 1·1099, and dissolves to the extent of 1 part in 88 parts of water; the Riedel-Pictet guaiacol has sp. gr. = 1·1171 at 24°, and dissolves in 80 parts of water; the residue from the above treatment has sp. gr. = 1·0889 at 24°, and dissolves in 200 parts of water. The three products yield 46 grams, 49 grams, and 8 grams of acetylguaiacol per 50 grams, respectively, when acetylised. Guaiacol purified in this manner does not become coloured when exposed to light, and is only feebly coloured by strong sulphuric acid.

A. G. B.

Aromatic Selenium Compounds. By P. CAMILLE CHABRIÉ (*Bull. Soc. Chim.*, 1894, [3], **11**, 1080—1083).—A criticism of Krafft and his collaborators (Abstr., 1894, i, 88, 448). The author has prepared various aromatic selenium compounds by synthesis with aluminium chloride. Phenylic hydroselenide is completely soluble in alcohol, and forms definite crystals melting at 60°; the analytical results, moreover, are in good agreement with those calculated from the formula PhSeH; it cannot, therefore, be a mixture of phenylic selenide and diselenide with selenium, as stated by Krafft. It is true that the analytical results agree equally well with those required by diphenylic diselenide, but it is not likely to be the latter, as it forms compounds with mercury analogous to the mercaptides. Diphenylic diselenoxide is an oily liquid boiling at 230° (65 mm.), and not a crystalline solid, as stated by Krafft; neither does it decompose into phenylic selenide when distilled. The dibromide melts at 120°. *Chlorodiphenylic selenoxide*, $C_6H_4Cl{\cdot}SePhO$, occurs as a bye-product in the aluminium chloride process; it crystallises well, and melts at 94°.

JN. W.

Manufacture of Orthonitraniline. By JOSEPH POKORNÝ (*Chem. Centr.*, 1894, ii, 556; from *Bull. Soc. Indust. Mulhouse*, 1894, 280—284).—Forty grams (?) of acetanilide is gradually added to 80 kilos. of sulphuric acid (66° B), while the liquid is well stirred and the temperature not allowed to rise above 50°; a mixture of 36 kilos. of nitric acid (36—37° B) with 40 kilos. of sulphuric acid (66° B) is allowed to flow into this solution of acetanilide, which is kept at a temperature of 40—50°, the application of cold and agitation being continued until the temperature of the liquid falls continuously. On the following day, the liquid is poured into 200 litres of hot water, whereon a yellowish precipitate, consisting of ortho- and paranitracetanilide is thrown down. To deacetylise the mixture, it is heated by steam until all the precipitate is dissolved; the liquor is then cooled to 50° and poured into 200 kilos. of ice which is kept well stirred. Orthonitraniline is thus precipitated, whilst paranitraniline may be thrown down from the mother liquor by mixing

it with 180 kilos. of soda-lye (36° B) and cooling with ice. The yield is 25 per cent. of ortho- and 60 per cent. of para-nitraniline.

A. G. B.

Action of Phthalic Chloride on Nitranilines. By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 1118—1120).—The results differ somewhat, especially as regards the melting points, from those of Dobreff (this vol., i, 360). With excess of phthalic chloride, nitrophthalanils, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_4\cdot NO_2$, are obtained; with excess of the nitraniline, nitrophthalanilides, $C_6H_4(CO\cdot NH\cdot C_6H_4\cdot NO_2)_2$; the numbers given are melting points.

Nitrophthalanils; 1 : 4, white, amorphous, 262—263°; 1 : 3, white, amorphous or crystalline, 242—244°; 1 : 2, yellowish needles, 200—203°. *Nitrophthalanilides;* 1 : 4, yellowish powder, 232—234°; 1 : 2, silky yellowish needles, 180—184°; 1 : 3 (?), 232—234°.

C. F. B.

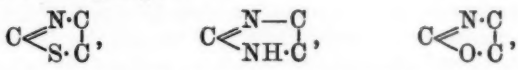
Derivatives of Benzylamine. By PAUL FRIEDLÄNDER and M. MOSCZYC (*Ber.*, 1895, **28**, 1140—1145).—1 : 4-*Dimethylamidobenzylamine*, $NMe_2\cdot CH_2\cdot C_6H_4\cdot NH_2$, is obtained by heating 1 : 4-nitrobenzylic chloride with dimethylamine in alcoholic solution, and reducing the product with stannous chloride; it is a colourless syrupy liquid, and boils with slight decomposition at above 300°; its *sulphate*, with H_2SO_4, crystallises in lustrous, yellowish plates. The corresponding *diethyl* compound boils at 212—214° under 40 mm. pressure. The methyl compound can be diazotised, and then yields with β-naphthol a basic azo-dye which crystallises in red needles and melts at 120°. It can also be converted by the diazo-reaction into the cyanide, the *platinochloride* of which was prepared.

If 1 : 4-toluonitrile is chlorinated at the boiling temperature, and the product treated with concentrated sulphuric acid, ω-chloro-1 : 4-toluamide is formed, and by warming this with aqueous dimethylamine, *ω-dimethylamine*-1 : 4-*toluamide* is obtained; this melts at 144°. Dilute alkalis convert it into the *acid*, $NMe_2\cdot CH_2\cdot C_6H_4\cdot COOH$, melting at 235°, the *platinochloride* of which melts at 220—224°; when reduced with sodium amalgam, the acid yields dimethylamine and paratoluic acid. ω-Chlorotoluic acid reacts with ω-dimethylamine-paratoluic acid, yielding *dimethylamidodibenzylparadicarboxylic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot CH(NMe_2)\cdot C_6H_4\cdot COOH$, which melts at 268—270°; the *hydrochloride* and *picrate* melt at 227° and 212° respectively. ω-Chloroparatoluamide is converted by sodium ethoxide into an *ethoxy-compound* which melts at 112°, and is hydrolysed by soda to *ω-ethoxyparatoluic acid*, $OEt\cdot CH_2\cdot C_6H_4\cdot COOH$, melting at 87°.

Paratoluic acid is converted by phosphorus pentachloride into the chloride, and when this is chlorinated at the boiling temperature, and that fraction of the product which boils at 265—270° treated with dimethylamine, ω-dimethylamidoparatoluic acid is obtained. The aniline derivatives prepared were $NHPh\cdot CH_2\cdot C_6H_4\cdot CO\cdot NHPh$, m. p. 183°; $NHPh\cdot CH_2\cdot C_6H_4\cdot CONH_2$, m. p. 150°; $NHPh\cdot CH_2\cdot C_6H_4\cdot COOH$, m. p. 50°.

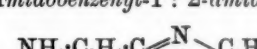
C. F. B.

Amido-derivatives of Benzenylamidophenols. By EUGEN LELLMANN and LUDWIG EBEL (*Ber.*, 1895, **28**, 1127—1129).—It has been already shown (Abstr., 1894, i, 79) that substances containing the second of the groups—



like those containing the first, are substantive colouring matters; it is now shown that compounds containing the third of these groups are also substantive dyes.

1 : 4- and 1 : 3-*Amidobenzenyl*-1 : 2-*amido*-1 : 4-*cresols*,



were obtained by reducing with stannous chloride the corresponding nitrotolylic salts of nitrobenzoic acids, themselves prepared by the action of 1 : 4- and 1 : 3-nitrobenzoic chlorides on nitrocresol [Me : NO_2 : OH = 1 : 3 : 4]. The 1 : 4-base crystallises in two different forms, which melt at 187° and 188°; the colourless 1 : 3-base melts at 143—144°. Both bases yield red substantive dyes when diazotised, and combine with β-naphthol, &c. C. F. B.

The Carbodiphenylimides. By WILHELM v. MILLER and JOSEF PLÖCHL (*Ber.*, 1895, **28**, 1004—1012).—Schall has described (Abstr., 1892, 1452) three isomeric carbodiphenylimides, the α- and β-compounds being, according to him, stereoisomerides, whilst the β- and γ-compounds are physical isomerides. The authors have repeated his experiments, and find that there are only two distinct substances, the empirical formulæ of which are the same, but that the β-modification has three times the molecular weight of the α-form, its molecular weight having been determined by the cryoscopic method in benzene solution. The γ-form appears to be simply a mixture of varying amounts of the α- and β-compounds. A. H.

Phenylimidocarbonates. By ARTHUR HANTZSCH and LUDWIG MAI (*Ber.*, 1895, **28**, 977—984).—Phenylimidocarbonates, $NPh{:}C(OR)_2$, are obtained by adding isocyanophenylchloride, $NPh{:}CCl_2$, (1 mol.) to a solution of a substituted sodium phenoxide (2 mols.) in ether and alcohol, and heating the mixture at 100°; when heated with strong hydrochloric acid, they yield aniline and carbonates, $CO(OR)_2$. If only 1 mol. of sodium phenoxide is used, phenylimidochloroformates, $NPh{:}CCl{\cdot}OR$, are obtained; when heated with alcohol, these yield phenylamidocarbonates (urethanes), $NHPh{\cdot}COOR$; and when heated with sodium derivatives of phenols, mixed phenylimidocarbonates, $NPh{:}C(OR'){\cdot}OR$ are formed. These last could not be shown to exist in geometrically isomeric forms, an identical product, $NPh{:}C(OPh){\cdot}OC_6H_4Br$, being obtained either by the action of $NaO{\cdot}C_6H_4Br$ on $NPh{:}CCl{\cdot}OPh$, or of NaOPh on $NPh{:}CCl{\cdot}OC_6H_4Br$. By these reactions the following substances were prepared; the numbers are melting points.

Phenylic phenylimidocarbonate, 136°. 1 : 4-*Bromophenylic phenyl-*

imidocarbonate, 106°; *di*-1 : 4-*bromophenylic carbonate*, 171°. *Phenylic phenylimidochloro-formate*, 42—45°; boils at 180° under 15 mm., at 199—200° under 22 mm. pressure. 1 : 4-*Bromophenylic phenylimidochloro-formate*, 45°; boils at 227° under 23 mm., at 223° under 22 mm. pressure; 1 : 4-*bromophenylic phenylamidocarbonate*, 144°; 1 : 4-*chlorophenylic phenylamidocarbonate*, 138°. *Phenylic* 1 : 4-*bromophenylic phenylimidocarbonate*, 83°.

Isocyanophenylchloride reacts with piperidine in ethereal solution as it does with aniline, and yields *phenyldipiperidylguanidine*, $NPh{:}C(NC_5H_{10})_2$, melting at 84°. The phenylimidochloro-formates (see above) also react with piperidine and with ammonia, yielding "isocarbamides," $NPh{:}C(NHR')\cdot OR$. Of these, *phenyl*-1 : 4-*bromophenylisocarbamide*, 142°, was prepared with ammonia; *diphenylpiperidylisocarbamide*, 86°, and *phenyl*-1 : 4-*bromophenylpiperidylisocarbamide*, 91°, with piperidine. C. F. B.

Preparation of Paraquinones from Indophenols. By Pierre H. Bayrac (*Bull. Soc. Chim.*, 1894, [3], **11**, 1129—1130).—Indophenol, $O{:}C_6H_4{:}N\cdot C_6H_4\cdot NMe_2$, and its homologues are hydrolysed by acids into dimethylparaphenylenediamine and quinone or homologues of the compound. The substance is merely dissolved in moderately strong sulphuric acid (7 parts of 40 per cent. acid), and the cooled solution extracted with ether. The product obtained on removing that solvent is then distilled with steam and recrystallised from a mixture of alcohol and ether. With the indoparaxylols, indocarvacrol, and indothymol, the yield of the quinone is quantitative, but with indophenol and the indocresols somewhat less, the stability of the molecule appearing to decrease as the number of groups attached to the benzene nucleus increases. Jn. W.

Indophenols. By Pierre H. Bayrac (*Bull. Soc. Chim.*, 1894, [3], **11**, 1131—1136).—The author has prepared several indophenols by the process used in the preparation of indothymol (Abstr., 1892, 1311), namely, by oxidising mixtures of dimethylparaphenylenediamine and the respective phenols with potassium dichromate in acetic acid solution, the diamine hydrochloride being prepared at the time by reducing paranitrosodimethylaniline hydrochloride with zinc dust. The yield is usually good.

The indophenols appear to crystallise in the triclinic system. They are practically insoluble in water, although the latter is coloured an intense blue by the trace dissolved, but they dissolve freely in the usual organic solvents yielding violet or blue solutions. As stated in the preceding abstract, they are hydrolysed by mineral acids into dimethylparaphenylenediamine and the respective quinones.

Dimethylanilquinonimide (indophenol), $O{:}C_6H_4{:}N\cdot C_6H_4\cdot NMe_2,\frac{1}{2}H_2O$, crystallises in steel-gray needles, and darkens at 100°, owing to the loss of its water of crystallisation; the anhydrous salt melts at 133—134°. *Dimethylanilorthotoluquinonimide* crystallises in rhombic needles, green by reflected light, and melts at 125°. The corresponding *meta*-compound crystallises in prisms, golden-yellow by reflected light, and melts at 117—118°. *Dimethylanilparaxyloquinonimide*,

$O:C_6H_2Me_2:N\cdot C_6H_4\cdot NMe_2$ (O : Me_2 : N = 1 : 2 : 5 : 4), crystallises in reddish-brown plates and melts at 125—126°. *Dimethylanilethylquinonimide*, $O:C_6H_3Et:N\cdot C_6H_4\cdot NMe_2$ (O : Et : N = 1 : 2 : 4), crystallises in long, rhombic plates, golden-yellow by reflected light, and melts at 83—84°. *Dimethylanilthymoquinonimide*, $O:C_6H_2MePr:N\cdot C_6H_4\cdot NMe_2$ (O : Me : Pr : N = 1 : 3 : 4 : 6), crystallises in triclinic, rhomboidal plates, also golden-yellow by reflected light, and melts at 87—88°.

JN. W.

Reduction of Aromatic Nitro-derivatives in Neutral Solution: Formation of Aromatic Hydroxylamines. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWITZ (*Bull. Soc. Chim.*, 1894, [3], **11**, 1038—1045; compare Bamberger, Abstr., 1894, i, 373, 412, and Wohl, *ibid.*, 409, 450).—Wohl and Bamberger's method of reducing nitro-compounds to β-hydroxylamines by means of zinc dust and water is not applicable to the nitrophenols and nitranilines, as these substances are completely reduced to the corresponding amidophenols and diamines by that reagent. The method, however, promises to be of commercial importance for the preparation of the latter bases, as the yield is extremely good, and the products pure. Ortho- and para-amidophenol and ortho- and para-phenylenediamine can be prepared in this way, and certain dinitro-compounds, such as dinitrobenzene, dinitronaphthalene, and 1 : 2 : 4-dinitrophenol, appear to undergo a similar reduction.

The homologues of nitrobenzene, on the other hand, readily yield substituted hydroxylamines, provided a small quantity of calcium or other chloride be present. *β-Paratolylhydroxylamine*, $C_6H_4Me\cdot NH\cdot OH$, crystallises from benzene in well-developed plates and melts at 92—93°. It is easily oxidised to paramethylazoxybenzene, azoxyparatoluene, or amidocresol, and is, of course, a powerful reducing agent. The *hydrochloride* crystallises in colourless needles. The *nitroso*-derivative, $NO\cdot C_6H_3Me\cdot NH\cdot OH$, forms colourless crystals and melts at 57—58°. *Additive compounds* with benzaldehyde and formaldehyde were also prepared; the benzaldehyde compound is crystalline and melts at 120°. Paratolylhydroxylamine may be used as a developer in photography. *β-Orthotolylhydroxylamine* is an oil having properties similar to those of the para-compound. *β-Paraxylhydroxylamine*, $C_6H_3Me_2\cdot NHOH$ (Me_2 : NHOH = 1 : 4 : 5), forms colourless crystals and melts at 88—89°. The *hydrochloride* crystallises in colourless plates. α-Nitronaphthalene yielded a liquid product having strong reducing properties, but nothing could be isolated from it but α-naphthylamine.

JN. W

Action of Hydroxylamine on Phthalic Anhydride. By GIORGIO ERRERA (*Gazzetta*, 1894, **24**, ii, 469—474).—*Hydroxylamine phthalylhydroxamate*, $OH\cdot NH\cdot CO\cdot C_6H_4\cdot COO\cdot NH_3\cdot OH$, is prepared by mixing alcoholic solutions of hydroxylamine hydrochloride and sodium ethoxide, separating the deposited sodium chloride and adding phthalic anhydride to the solution; the salt separates as a colourless, crystalline substance soluble in water; its solutions give a red coloration with ferric chloride, and reduce Fehling's solution. It decomposes at 130—135°, yielding phthalylhydroxylamine, hydroxyl-

amine, and water; ammonium phthalylhydroxamate is also formed as a product of secondary action.

By employing a smaller proportion of hydroxylamine than that used in the above preparation, sodium phthalylhydroxamate is obtained. W. J. P.

Isomerism in the Azo-series. By ARTHUR HANTZSCH (*Ber.*, 1895, **28**, 1124—1126).—The compounds obtained by Bamberger (this vol., i, 351) from nitrodiazobenzene salts and α-naphthol are not, as he thinks, stereochemically isomeric, but are structurally isomeric, the $\cdot N_2 \cdot C_6H_4 \cdot NO_2$ group occupying, in the α- and β-compound respectively (melting at 277—279° and 235°), the 4- and 2-positions with respect to the OH of the naphthol. This is shown by the fact that the two compounds, when reduced with stannous chloride, yield respectively 4 : 1- and 2 : 1-amidonaphthol. C. F. B.

Methylphenyldithiobiuret and Methylphenylthiuret. By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1096—1101; compare Abstr., 1893, i, 575).—*Methylphenyldithiobiuret* (*biuramine*) was prepared by heating methylaniline with perthiocyanic acid, $C_2H_2N_2S_3$, at 100°; it forms white crystals, melts at 156°, and dissolves in alkalis, but not in dilute acids. When it is oxidised with iodine, it reacts as if it had the constitution $NMePh \cdot C(SH):N \cdot C(SH):NH$, and yields *methylphenylthiuret*, $NMePh \cdot C<\begin{matrix}S\\N\end{matrix}>C:NH$. This substance could not be isolated, but it acts as a monacid base, and its *hydrochloride*, *hydrobromide*, and yellow *hydriodide* melt respectively at 232°, 220°, and 193°; when boiled with aqueous potash, it yields ammonia and methylaniline. C. F. B.

Condensation of Methylphenyldithiobiuret with Aldehydes and Ketones. By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1102—1113).—When methylphenyldithiobiuret (compare preceding abstract) is mixed with an aldehyde or ketone, O:CXR, and hydrogen chloride passed into the mixture, it reacts as if it had the constitution $NMePh \cdot CS \cdot NH \cdot CS \cdot NH_2$, and yields compounds $NMePh \cdot CS \cdot N<\begin{matrix}CS\\CXR\end{matrix}>NH$. With acetone, it yields *α-methylphenyldithio-dimethylketuret*, melting at 152°; with benzaldehyde, *α-methylphenyldithiophenylalduret*, melting at 168°; with acetaldehyde, the reaction is anomalous. When the above-mentioned keturet and alduret are dissolved in cold alcoholic soda, and the solutions allowed to remain with benzylic chloride, *monobenzyl derivatives* are formed, melting respectively at 85° and 127°. When these are heated on the water bath with strong hydrochloric acid, they are decomposed; the keturet yields, besides methylaniline, ammonia, carbonic anhydride, hydrogen sulphide, benzylic hydrosulphide, and bisulphide, some acetone and benzylic imidotrithiodicarboxylate,

$$CSS(C_7H_7) \cdot NH \cdot COSC_7H_7,$$

doubtless formed by the action of benzylic hydrosulphide on the compound $CSOH \cdot NH \cdot COSC_7H_7$ first formed. In the case of the

alduret, the last compound is not formed; benzaldehyde is liberated in place of acetone, and benzylic hydrosulphide reacting more readily with it than it does with acetone, the compound $C_6H_5{\cdot}CH(SC_7H_7)_2$ is obtained, and no benzylic imidotrithiodicarboxylate. This substance is however obtained, together with the compound mentioned, if excess of benzylic hydrosulphide is present from the beginning of the reaction. *Benzylic imidotrithiodicarboxylate* crystallises in yellowish needles, and melts at 144—145°; when treated with alcoholic ammonia, it yields monothiobiuret. C. F. B.

Combination of Benzaldehyde with Hydrocyanic acid in Dilute Solution. By E. Utescher (*Chem. Centr.*, 1894, ii, 675—676; from *Pharm. Post*, **27**, 417—421).—Contrary to Glücksmann the author maintains that the combination of benzaldehyde with hydrogen cyanide is a very rapid process even in dilute solution. Benzaldehyde was mixed with hydrocyanic acid and alcohol in the proportion of 1 part of the acid to 6 parts of the aldehyde, the solution containing 0·1 per cent. of hydrogen cyanide in one experiment and 0·2 per cent. in another. In the case of the 0·2 per cent. solution, 0·0845 per cent. of acid was left uncombined after 60 hours, 0·0245 per cent. after five days, and 0·0137 per cent. after 10 days. In water with 0·1 per cent. of hydrogen cyanide, the combination is more gradual. The author has already shown that benzaldehyde cyanhydrin is not completely decomposed by dilute potash. Hydrogen cyanide which has been mixed with excess of ammonia, then with excess of nitric acid, and with N/10 silver nitrate solution, shows when titrated by Volhard's method a lower content of hydrogen cyanide the longer the time which is allowed to elapse between the addition of the nitric acid and of the silver nitrate; thus, in a quarter of an hour the amount indicated dropped from 0·503 per cent. to 0·495 per cent. Glücksmann used a hydrocyanic acid solution of about half this strength; he also employed too small a proportion of benzaldehyde. A. G. B.

Condensation of Mandelic acid with Phenols. By Augustin Bistrzycki and J. Flatau (*Ber.*, 1895, **28**, 989—991).—When mandelic acid (5 parts) is heated with phenol (7 parts) in the presence of 73 per cent. sulphuric acid (20 parts), a compound is formed which is probably *hydroxydiphenylacetic lactone*, $CHPh<^{C_6H_4}_{CO-}>O$; the yield is 22 per cent. of the theoretical. The lactone melts at 113—114°, and boils at 337°; when boiled with aqueous sodium carbonate, it yields the sodium salt of the *acid*, which itself melts at 85—87°. In a similar manner *phenyl*-1 : 4-*cresylacetic acid* and its *lactone* were obtained from mandelic acid and 1 : 4-cresol; they melt at 118° and 106° respectively. C. F. B.

Coumarincarboxylates and a New Synthesis of Coumarin. By Pietro Biginelli (*Gazzetta*, 1894, **24**, ii, 491—503).—*Ethylic metahydroxycoumarin-β-carboxylate*, $\begin{matrix} C(OH){:}CH{\cdot}C{\cdot}C(COOEt){:}CH \\ CH = CH{\cdot}CO\text{———}CO \end{matrix}$, is

obtained by adding concentrated sulphuric acid to a solution of quinol in ethylic oxalacetate; it exists in two modifications which are separated by crystallisation from alcohol and ether; the least soluble modification crystallises in yellow laminæ melting at 177—178°, whilst the more soluble crystallises in yellow prisms melting at 180—182°. The former isomeride may be converted into the modification of higher melting point by boiling with dilute alcohol, and the author concludes that they are stereoisomerides. The ethylic salts are accompanied by small quantities of the free *acids* which are, however, best prepared by hydrolysing these salts with potash, adding acid, and crystallising from water; the one acid crystallises in thin, yellow needles melting at 279—280°, whilst the other forms acicular laminæ melting at 283—284°. When heated at 280—290°, the acids distil with partial decomposition, and are deposited in yellow laminæ melting at 289°. The *sodium* salt crystallises from water in needles containing $1H_2O$, which is lost at 100°, but is deposited from alcohol in prisms containing $\frac{1}{2}H_2O + \frac{1}{2}EtOH$; the salt is very soluble in water, and, on treatment with acids, yields the acid melting at 280°.

Although carbonic anhydride is evolved on heating the above acid, the hydroxycoumarin cannot be isolated from the residue, and can only be prepared from the acid by the process described below.

Methylic metamethoxycoumarin-β-carboxylate, $OMe{\cdot}C_9H_4O_2{\cdot}COOMe$, is obtained by treating the above acid in methylic alcoholic potash solution with methylic iodide; it crystallises in needles, melts at 131—132°, and is readily hydrolysed by alkalis yielding the corresponding *acid*, which crystallises in yellow laminæ melting at 246—247°. On heating the acid with iron dust, or its sodium salt with caustic soda, the metamethoxycoumarin melting at 102—103° is obtained; on treatment with hydriodic acid, it yields the metahydroxycoumarin melting at 249°. W. J. P.

Triacetylgallic acid. By Paul Cazeneuve (*Bull. Soc. Chim.*, 1894, [3], **11**, 937).—A reply to Schiff (this vol., i, 368).

Triacetylgallic acid. By Paul Sisley (*Bull. Soc. Chim.*, 1894, [3], **11**, 938—939).—Boettinger's triacetylgallic acid (Abstr., 1884, 1178) is identical with the author's diacetylgallic acid (this vol., i, 283). Boettinger's pentacetyltannin (*loc. cit.*) is identical with the triacetylgallic acid of Schiff and the author (*loc. cit.*).

As diacetylgallic acid does not give a colour reaction with ferric chloride, the absence of a coloration with that reagent must not be taken as conclusive evidence of the absence of phenolic hydroxyl from the molecule. Jn. W.

Hemipinic acid and its Ethereal Salts. By Rudolf Wegscheider (*Monatsh.*, 1895, **16**, 75—152; compare Abstr., 1882, 1206, and 1891, 712).—Hemipinic acid, $C_6H_2(OMe)_2(COOH)_2 = [1:2:3:4]$, is most readily obtained by treating opianic acid oxime with potash, or by oxidising opianic acid itself with potassium permanganate. This acid appears to exist in only one modification; the different melting points, varying from 160° to 178°, given by different authori-

ties, are due to the fact that it is partially converted into the anhydride even before it melts. The amount of anhydride thus formed depends on the length of time during which the acid is heated, and consequently the melting point also varies with the rate of heating.

The monalkylic salts of hemipinic acid form two isomeric series, the α and β, the normal alkylic salts only one.

	Methylic.	Ethylic.	Normal propylic.
Normal salt, m. p. =	61— 62°	72°	43—45°
α-acid salt, m. p. =	121—122	144·0—145°	119·0—120·0° and 131—132·0°
β-acid salt, m. p. =	137—138	147·5—149	111·5—112·5 and 125—125·5

The α-monethylic and both α- and β-monopropylic hemipinate occur in desmotropic forms. The two α-ethylic salts have the same melting point, but differ in other physical properties. The propylic salts have the melting points given above.

All the monalkylic salts when heated yield hemipinic anhydride and the corresponding alcohol.

The *α-ethereal salts* are best obtained—(1) By the oxidation of the true ethereal salts of opianic acid. (2) By boiling hemipinic anhydride with the requisite alcohol; a small quantity of the β-salt is also formed in this reaction. (3) By heating potassium hydrogen hemipinate with alcohols and alkylic iodides; this reaction is, however, incomplete. (4) By the hydrolysis of the normal ethereal salts.

The α-ethereal salts give a yellow coloration and milky turbidity with very dilute ferric chloride solution.

The isomeric *β-derivatives* are best obtained by saturating a solution of the acid in alcohol with dry hydrogen chloride. The β-salts are the first products formed, but if the saturation is carried out for several hours at the boiling point of the alcoholic solution, normal salts are also obtained, and these, in the presence of the hydrogen chloride, become hydrolysed to the α-salts.

The silver salts of both α- and β-derivatives, when heated at 200—230° under a pressure of 21 mm., are decomposed, and yield ethylic veratrate, together with hemipinic acid.

The α-salts have the constitution $C_6H_2(COOH)(COOA)(OMe)_2$ [1 : 2 : 3 : 4], since they are obtained by the oxidation of the corresponding opianates; and the constitution

$$C_6H_2(COOA)(COOH)(OMe)_2\ [1 : 2 : 3 : 4],$$

for the β-series follows from the law of V. Meyer and Sudborough. The author discusses the theories of Friedel and of Henry, regarding the etherification of acids, by means of alcohol and hydrogen chloride, in the light of the recent observations of Meyer and Sudborough. Henry's hypothesis, according to which the etherification is preceded by the addition of the elements of the alcohol to the carbonyl group of the acid, is considered the more probable. It may be, however, that it is the hydrogen chloride and not the alcohol which unites with the carbonyl group. The presence of substituting groups in the ortho-positions may thus prevent the formation of such additive compounds, just as according to Meyer and Sudborough's theory such

groups can prevent the direct entry of alkyl radicles. If this is true, then we must expect to meet similar phenomena in the formation of imido-ethers, amidines, and amidoximes. Similarly diortho-substituted aldehydes should be incapable of taking part in reactions which require the formation of additive compounds.* Hemipinic and camphoric acids exhibit very similar phenomena when etherified, but as the constitution of camphoric acid has not been definitely determined, the two series cannot be very closely compared. It can be shown, however, that the etherification does not depend on the strength of the carboxylic group, as in hemipinic acid the weaker carboxylic group is the first to be etherified, but in camphoric acid the reverse is true. By the action of alkalis on the normal ethereal salts of both acids, the first carboxylic group to be hydrolysed is the one which is the first to be etherified. J. J. S.

Preparation of Ethylidenediphenylsulphone. By Robert Otto and K. Mühle (*Ber.*, 1895, **28**, 1120—1122).—*Ethylidenediphenylsulphone* (Escales and Baumann, Abstr., 1887, 123) can be conveniently prepared by oxidising ethylidenedithiophenyl, prepared from ethylidenic dichloride and sodium thiophenoxide (*J. pr. Chem.*, [2], **51**, 518), with permanganate in acetic acid solution, and removing the admixed manganese oxide with sulphurous anhydride. C. F. B.

Derivatives of Benzylideneacetophenone. By Carl Goldschmidt (*Ber.*, 1895, **28**, 986).—Benzylideneacetophenone yields two *oximes*, melting respectively at 68° and 140°; the latter is gradually transformed into the former when kept. It also yields two *nitroderivatives;* one melts at 159°, the other is an oily 1 : 2-derivative, which yields 2′-phenylquinoline when reduced with stannous chloride. C. F. B.

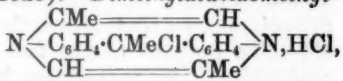
Paratoluoylorthobenzoic acid and Benzophenonedicarboxylic acid. By Heinrich Limpricht (*Ber.*, 1895, **28**, 1134—1135).—Paratoluoylorthobenzoic acid could not be obtained crystallised with H_2O, as Friedel and Crafts describe it; the melting point, further, was 138—139° instead of 146°. When oxidised with permanganate, it yields *benzophenonedicarboxylic acid*, $CO(C_6H_4\cdot COOH)_2$, which crystallises with H_2O and also anhydrous; the anhydrous acid melts at 239°, its *methylic salt* at 107°. With acetic anhydride, the acid yields a *diacetyl derivative*, melting at 182°. The *acid chloride* melts at 110°, and, when treated with zinc-ethyl in ethereal solution, yields the *ketone*, $CO(C_6H_4\cdot CO\cdot C_2H_5)_2$, which melts at 105°. C. F. B.

A Colour Reaction of Carbazole. By Giacomo Carrara (*Gazzetta*, 1894, **24**, ii, 535—540).—On heating carbazole (1 mol.) with salicylaldehyde (2 mols.) and concentrated sulphuric acid at 100—110°, an intensely blue product is obtained; it contains, in addi-

* V. Meyer (*Ber.*, 1895, **28**, 1267) has shown that this is probably true for Perkin's reaction.—J. J. S.

tion to carbazolemono- and di-sulphonic acids, an amorphous reddish colouring matter, which forms a barium salt, contains much sulphur, and is soluble in water, alcohol, ether, and benzene. It dyes mordanted silk and cotton, and is still under investigation.

W. J. P.

New Series of Colouring Matters. By CHARLES FRIEDEL (*Bull. Soc. Chim.*, 1894, [3], **11**, 1027—1028).—*Dimethyldiazidomethyldiphenylchloromethane hydrochloride*,  , formed by the action of phosphoric oxychloride on methylacetanilide at 120°, is probably a condensation product of methylacetanilide with its acetyl derivative, as hydrogen chloride and methylaniline are eliminated in the reaction. It crystallises from alcohol, in which it dissolves to a crimson solution, in small needles, which are blue by reflected and red by transmitted light. As the *dihydrochloride* is practically colourless, the base promises to be of use as an indicator in alkalimetry, for the acid solution is coloured crimson even by aniline; the colour is discharged, however, by carbonic anhydride and acetylacetone, although it is not affected by phenol. The hydrochloride dyes wool and silk as well as cotton mordanted with tannin, but the colour, although unaffected by soap, is not very fast to light, and is of course discharged by acids.

When the hydrochloride is boiled with alkali sulphites, it is converted into the *sulphite* $C_{20}H_{20}N_2SO_3$, a substance crystallising in small, golden, rhomboïdal plates having a greenish metallic lustre; this is insoluble in water, but soluble in hot alcohol, yielding a violet solution, and is decomposed by hydrochloric acid. The *benzoate* crystallises in small needles having a greenish, metallic lustre. The *nitrate* and *acetate* are also coloured.

When a stream of air is passed through the boiling hydrochloric acid solution of the sulphite, the latter is converted into *dimethyldiazidomethyldiphenylmethylic oxide*, $(C_{20}H_{20}N_2)_2O,H_2O$, which is precipitated in crimson flakes by caustic alkalis, and crystallises from alcohol in orange prisms. The *sulphate* of this oxide,

$$(C_{20}H_{20}N_2)_2O,4H_2SO_4,8H_2O,$$

crystallises in colourless, rectangular plates, and is rose-coloured when anhydrous. The oxide is reconverted into the original chlorinated base by the action of phosphoric oxychloride in benzene solution, but by the prolonged action of this reagent is transformed into a *blue colouring matter*, which is also formed from the original hydrochloride by oxidation with air in presence of alkali.

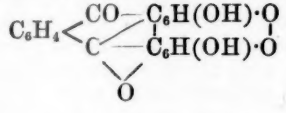
On distilling the hydrochloride with zinc dust, a *leuco-base*, $C_{20}H_{22}N_2$ or $C_{20}H_{24}N_2$, is obtained as a colourless oil, boiling at about 260°. The *platinochloride* of this base was prepared. JN. W.

Coloured Sulphonic Derivatives of Triphenylmethane. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], **11**, 1188—1190).—Solutions of "acid rosaniline," $OH\cdot C[C_6H_3(SO_3Na)\cdot NH_2]_3$, and other sulphonated colouring matters of the same type, are decolorised by

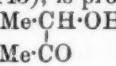
caustic alkalis, but quickly regain their colour on the addition of ammonium chloride. Rosenstiehl's view that the free substance is alcoholic and colourless does not offer any explanation of these facts, and is, in fact, in direct contradiction to them. If, however, it be granted that the free substance is acidic and coloured, whilst its sodium salt is colourless, an explanation is at once forthcoming. The ammonium salt, like the sodium salt, will be colourless, but prone to dissociation, so that, when the ammonium chloride is added, a considerable amount of the free acid will be liberated, and the colour restored. If this assumption be true, a solution of the dye, which has been decolorised by excess of ammonia, should tend to regain its colour on heating, but lose it again on cooling, unless the ammonia has been expelled by the heat, and this is actually the case. A further confirmation is found in the behaviour of an alkaline solution to which an equivalent amount of ammonium chloride has been added; on evaporating the solution to dryness, the residue, which can contain nothing but sodium chloride and the free hydroxylic substance, or its anhydride, regains the colour of the dye.

JN. W.

Cœruleïn. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], **11**, 1136—1138).—When cœruleïn is fused with aniline hydrochloride, a blue colouring matter is formed, which dyes bluish-green with iron and chromium mordants, and blue with those of aluminium. The condensation can be effected with the base itself by heating with a slight excess until the product appears to be dry, 2 mols. of aniline entering into combination, and 2 mols. of water being eliminated. The *condensation product*, after removal of the excess of aniline at 180°, is a violet powder, brownish-red by reflected light. It is sparingly soluble in water, but easily in concentrated sulphuric acid to a solution, which is blue when diluted, and from which the base is precipitated in greenish flocks by alkalis. The *acetate* dyes mordanted cotton greenish-blue, and wool and silk blue without mordants, but the colours are not fast to soap, owing to the liberation of the greenish base by the alkali. The base does not combine with the mordants of the aluminium group, so that its molecule does not contain hydroxyl. Since 2 mols. of water are eliminated in the condensation, it is probable that the cœruleïn molecule contains two hydroxyl groups; and as it also contains a phenylanthranol nucleus, its constitution may possibly be represented by the formula



JN. W.

1 : 4-Dimethylnaphthol. By STANISLAO CANNIZZARO and AMERICO ANDREOCCI (*Gazzetta*, 1895, **25**, i, 53—59).—The oxidation product of the dimethylnaphthol obtained by the decomposition of santanous acid (Abstr., 1894, i, 143), is probably an oxydimethylnaphthol of the constitution  ; it yields a crystalline *oxime* which

melts at 175°, and a *monhydrazone*, crystallising in long, red needles melting at 83—84°, and, on reduction, yields the original dimethylnaphthol. On treatment with hydrochloric acid, the oxime yields a green crystalline *anhydride*, which is converted into a stable and volatile *isomeride* by alcoholic potash; this substance crystallises in red needles and melts at 173°.

An *acetyldimethylnaphthylamine*, $C_{10}H_5Me_2{\cdot}NHAc$ [= 1 : 4 : 2], is obtained by heating the dimethylnaphthol with acetamide under pressure; it crystallises in small, colourless prisms melting at 218—220°. On hydrolysis with sodium ethoxide at 150°, it yields the corresponding *dimethylnaphthylamine*, which crystallises in colourless prisms melting at 74°, boils at 333° under 745 mm. pressure, and gives the above acetyl derivative with acetic anhydride. On oxidation with permanganate, the amine yields an *azodimethylnaphthalene*, which crystallises in small, red needles melting at 253°; it is accompanied by a colourless, crystalline *acid*, still under examination.

W. J. P.

Phenolnaphthaleïn. By George F. Jaubert (*Ber.*, 1895, **28**, 991—994).—Although phenol and naphthalic anhydride do not condense when heated together in the presence of most dehydrating agents, they do so when aluminium chloride is the agent used. The product, *phenolnaphthaleïn*, $CO<^{-O-}_{C_{10}H_6}>C(C_6H_4{\cdot}OH)_2$ [CO : C = 1 : 1′], is a white substance, and melts and decomposes at 120° when amorphous, and at 200° when crystalline; its solution in alkalis has a red colour, with rather more of a bluish shade than is the case with phenolphthaleïn. With phosphorus pentachloride, it yields a *chloride*, $C_{21}H_{14}O_2Cl_2$, melting at 180°; with hydroxylamine, a yellowish *oxime* melting at 220°.

C. F. B.

Action of Carbamide on Quinones. By Siro Grimaldi (*Gazzetta*, 1895, **25**, i, 78—79).—Phenanthraquinone and carbamide readily interact, giving two crystalline *compounds*, the one of which, $C_{15}H_{10}N_2O_2$, melts at 299°, whilst the other, $C_{16}H_{12}N_4O_2$, does not melt at 320°, and yields a crystalline *dinitro*-derivative, $C_{16}H_{10}N_4O_2(NO_2)_2$. With thiocarbamide and ammonium thiocyanate, phenanthraquinone yields a *dithioureïde*, $C_{16}H_{12}N_4S_2$. β-Naphthaquinone reacts with carbamide, forming a *monoureïde*, $C_{11}H_8N_2O_2$; anthraquinone similarly yields a *monoureïde*, $C_{15}H_{10}N_2O_2$, whilst quinone gives a crystalline *monoureïde*, $C_7H_6N_2O_3$, which does not melt at 320°.

W. J. P.

Essence of Cananga. By Albert Reychler (*Bull. Soc. Chim.*, 1894, [3], **11**, 1045—1051).—Cananga oil from Java has a sp. gr. = 0·9058 at 21°, a refractive index, $\mu = 1{\cdot}49655$, and a specific rotatory power, $[\alpha]_D = -28{\cdot}5°$. The proximate constituents appear, on the whole, to be the same as those of essence of Ylang-ylang (this vol., i, 294), but their relative amounts are different. Thus, on hydrolysis, the cananga essence also yields acetic and benzoic acids, but only in small proportion, whilst a relatively large amount of volatile oil is obtained; this, again, contains but a small quantity of the alcoholic substance, the major portion consisting of a sesquiterpene.

The *sesquiterpene* boils at 252—257°; the sp. gr. = 0·9024 at 17°; the specific rotatory power, $[\alpha]_D = -32·2°$ at 20°; the refractive index, $\mu = 1·50187$ at 17°. The molecular refraction = 66·8, and the iodine number = 255, so that two ethylene linkings are present in the molecule. The specific rotatory power, like that of other sesquiterpenes, is diminished, or even reversed, by heating at temperatures above 250°.

The *alcohol*, $C_{10}H_{18}O$, boils at 98—102° (20—21 mm.); the molecular refraction = 48·81, so that two ethylene linkings are present in the molecule, a conclusion confirmed by the iodine absorption.

Amongst the other substances isolated was an *oil* boiling at 166—173°, which, on oxidation with chromic acid mixture, yielded an acid, $C_9H_{10}O_3$, probably anisic acid.

Heine and Co., in a communication to the author, state that in addition to ylangol, they have isolated from essence of Ylang-ylang either geraniol, or some isomeride of that substance. JN. W.

Action of Nitrous acid on Oximes of the Camphor (Camphane) Series. By ANGELO ANGELI and E. RIMINI (*Ber.*, 1895, **28**, 1077—1078).—Camphoroxime, in glacial acetic acid solution, reacts with sodium nitrite; the product, $C_{10}H_{16}N_2O_2$, is crystalline, and melts at 43°. Camphenoxime yields a similar compound, $C_{10}H_{14}N_2O_2$, which melts at 47°. Both substances are insoluble in acids and alkalis, and neither of them gives Liebermann's reaction. Menthoneoxime appears to react with sodium nitrite in a similar manner (compare following abstract). J. B. T.

Conversion of Camphor into an Isomeric Unsaturated Compound. By ANGELO ANGELI (*Ber.*, 1895, **28**, 1127).—The compound $C_{10}H_{16}N_2O_2$, obtained (preceding abstract) by the action of nitrous acid on camphoroxime, is attacked by cold strong sulphuric acid, a gas being evolved and a compound, $C_{10}H_{16}O$, isomeric with camphor, formed. This is an oily liquid, and yields an *oxime* melting at 106°. Both ketone and oxime immediately decolorise permanganate, and are therefore unsaturated compounds. C. F. B.

Camphor. By FERDINAND TIEMANN (*Ber.*, 1895, **28**, 1079—1093). —*Camphorimine nitrate*, $C_{10}H_{16}NH,HNO_3$, is formed by the action of nitrous acid on camphoroxime; it is crystalline, and melts at 156°. *Camphorimine* is also crystalline, melts above 90°, evolves ammonia, and yields a number of decomposition products when exposed to air; it readily forms salts with acids, most of which are crystalline, and from them camphor may be regenerated. By the action of methylic iodide, *methylcamphorimine hydriodide*, $C_{10}H_{16}NMe,HI$, is formed.

Camphenylnitramine, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NH\cdot NO_2\end{matrix}$, is formed, along with the imine; with alcoholic potash, it readily yields a crystalline *potassium* salt, which explodes violently on heating, and yields camphoric acid when oxidised with potassium permanganate. Determinations of its refractive power show that it contains a double linking (com-

pare preceding abstracts). By the action of hydriodic acid, camphor is formed; with ammonia, camphorimine is regenerated. The reaction has been studied in the case of other ketones and aldehydes; these differ both in the yield and also in the manner in which their oximes react with nitrous acid, but the method may be employed with advantage to convert isonitrosocamphor into camphorquinone.

Camphoroxime is readily converted into campholenonitrile by the action of dehydrating agents (sulphuric acid, hydriodic acid), and this easily yields the amide by fusion with potash; when boiled with potash, it gives the amide and acid successively. The oxime and amide are lævogyrate, the nitrile and acid, like the original camphor, dextrogyrate. When the α-nitrile is hydrolysed with acids and the product treated with alkali, *isamidocamphor*, $C_{10}H_{15}O{\cdot}NH_2$, is formed; it is a saturated primary base, extremely stable towards alkalis, readily changed by acids, has an unpleasant odour, is crystalline, melts at 39°, and boils at 254—256° under normal pressure, and at 152° under 65 mm. pressure. The *salts* crystallise readily, and, when their solutions are heated, β-campholenamide, $C_{10}H_{17}NO$, is precipitated; this is also formed by the action of ammonia on β-campholenic acid (m. p. 52°), it melts at 86°, regenerates the acid by treatment with potash, and has been recently described by Béhal (this vol., i, 241); he appears to have prepared it from a mixture of the α- and β-nitriles; of these, the latter is more readily hydrolysed by potash than the former; his nitrile, regenerated from the hydrogen iodide derivative, yields a mixture of α- and β-amide (m. p. 92°). α-Campholenonitrile is readily prepared by heating camphoroxime with sulphuric acid (20 per cent.); it boils at 225°. β-Campholenonitrile is best obtained by the prolonged heating of camphoroxime with dilute hydriodic acid; it boils at 217°. No optically active β-campholene derivatives have been prepared.

Hydroxydihydrocampholenolactone, $C_{10}H_{16}O_2$, is formed when isamidocamphor hydrochloride is allowed to remain for some time in aqueous solution at the ordinary temperature; it is also obtained by heating α- or β-campholenic acid with strong acids; it boils and undergoes partial decomposition at 255°, is insoluble in water and soda at ordinary temperatures, and is not changed by boiling with water and calcium carbonate or, in ethereal solution, by treatment with ammonia. A *bromine derivative* is formed by the interaction of β-campholenic acid and bromine.

Hydroxydihydrocampholenic acid, $C_{10}H_{18}O_3$, crystallises in lustrous, colourless needles, melts at 105°, and is stable when pure, but traces of foreign substances cause its rapid conversion into the lactone. When quickly hydrolysed with alcoholic potash, the lactone is frequently converted into campholene, but the pure acid and α- and β-campholenic acids are very stable towards alkalis; statements to the contrary made by various observers are due to the use of acids containing a little lactone; the varying descriptions given of α- and β-campholenic acids is due to the same cause, since a trace of mineral acid suffices to convert α-campholenic acid into the lactone, and the latter always yields some β-campholenic acid when distilled. Attention is drawn to the considerable alterations in boiling and melting

point produced in campholene derivatives caused by the presence of traces of impurity.

In discussing the constitution of camphor, exception is taken to Bredt's formula on the ground that it does not satisfactorily explain the behaviour of camphoroxime as a syn-derivative; if Bredt's formula is correct, the oxime should contain the complex $\begin{matrix}\text{CMe}\cdot\text{C}\cdot\text{CH}_2\\ \|\\ \text{N}\cdot\text{OH}\end{matrix}$ and campholenic acid, campholic acid, and camphoric acid should have the formulæ $CH_2{:}C_8H_{13}\cdot COOH$, $C_8H_{14}Me\cdot COOH$, and $C_8H_{14}(COOH)_2$ respectively, they ought, therefore, to yield similar decomposition products, and campholenic acid should be readily converted into the other acids. To overcome this objection, the formula $CH\begin{matrix}\diagup\text{CH}_2\text{---CO}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe}_2\cdot\text{CHMe}\diagup\end{matrix}CH$ is suggested for camphor; its conversion into cymene is preceded by the formation of a dihydrocarvone, $CHPr^{\beta}\begin{matrix}\diagup\text{CH}_2\cdot\text{CO}\diagdown\\ \diagdown\text{CH}_2\cdot\text{CH}\diagup\end{matrix}CMe$. The corresponding formula for fenchone, $CH\begin{matrix}\diagup\text{CH}\cdot\text{CHMe}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe---CO}\diagup\end{matrix}CH$, obtains support from Wallach's work (*Annalen*, 1895, **284**, 341).

For camphene and pinene, the formulæ $CH\begin{matrix}\diagup\text{CH}\text{=}\text{=}\text{CH}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe}_2\cdot\text{CHMe}\diagup\end{matrix}CH$ and $CH\begin{matrix}\diagup\text{CH}_2\text{---CH}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe}_2\cdot\text{CHMe}\diagup\end{matrix}C$ respectively are deduced; the latter is in complete accord with investigations by the author and F. W. Semmler, which will be published shortly. The formulæ of the more important compounds referred to above are as follows.

$\text{COOH}\cdot\text{CH}_2\cdot\text{CH}\begin{matrix}\diagup\text{CH}\text{=}\text{CH}\diagdown\\ \text{CMe}_2\cdot\text{CHMe}\end{matrix}$; $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}\begin{matrix}\diagup\text{CH}_2\text{---CH}\diagdown\\ \text{CMe}_2\cdot\text{CMe}\end{matrix}$;

α-Campholenic acid. β-Campholenic acid.

$\text{CH}\begin{matrix}\diagup\text{CH}_2\text{---CO}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe}_2\cdot\text{CHMe}\diagup\end{matrix}\text{CNH}_2$; $\text{CH}\begin{matrix}\diagup\text{CH}_2\text{---CO}\cdot\text{O}\diagdown\\ \text{CH}_2\\ \diagdown\text{CMe}_2\cdot\text{CHMe}\diagup\end{matrix}\text{CH}$;

Isamidocamphor. Dihydrocampholenolactone.

$\text{CHMe}\begin{matrix}\diagup\text{CH}_2\text{---CH}\cdot\text{COOH}\diagdown\\ \text{CMe}_2\cdot\text{CHMe}\end{matrix}$; $\text{COOH}\cdot\text{CH}\begin{matrix}\diagup\text{CH}_2\text{---CH}\cdot\text{COOH}\diagdown\\ \text{CMe}_2\cdot\text{CHMe}\end{matrix}$.

Campholic acid. Camphoric acid.

In a supplementary note, Béhal's later communication (this vol., i, 241) is summarised and discussed. Béhal regards the campholenic acids as stereoisomeric, although unable to prepare an optically active form of the β-acid; the author points out that, although according to the above formula it contains an asymmetric carbon atom, the optical activity is lost as soon as a compound of the α-series is converted into the β-series, even though haloïd acids are excluded; he considers

that this supports his formula, and shows that the optical activity is dependent on the asymmetry or otherwise of the carbon atom in the CMe group. J. B. T.

Derivatives of Quercetin. By CARL T. LIEBERMANN (*Monatsh.*, 1895, **16**, 180—182).—A reply to J. Herzig's criticisms on some of the author's previous analyses (Abstr., 1884, 1365). It is shown that these old analyses agree very well with the new formula, $C_{15}H_{10}O_7$, suggested for quercetin by Herzig. J. J. S.

Action of Potassium Permanganate and of Hydriodic acid and Red Phosphorus on Rottlerin. By PIETRO BARTOLOTTI (*Gazzetta*, 1894, **24**, ii, 480—484; compare Abstr., 1894, i, 301).—Rottlerin is readily oxidised by alkaline permanganate in the cold with formation of benzoic and oxalic acids; chromic acid attacks rottlerin very slowly, and only very little benzoic acid is formed.

Resinous products are obtained on heating rottlerin with hydriodic acid in sealed tubes at 210—220°, but, on heating at the same temperature with hydriodic acid and red phosphorus, a pleasant-smelling oil, lighter than water, is formed; it boils at 140—240°, and the fractions boiling at 140—150° and at 230—240° have the same composition, namely $C_{10}H_{16}$ or $C_{11}H_{18}$. The examination of this oil is being continued. W. J. P.

Yeast Glucase. By CARL J. LINTNER and E. KRÖBER (*Ber.*, 1895, **28**, 1050—1056).—Dried yeast, when extracted with water at ordinary temperatures, yields an enzyme which readily hydrolyses maltose; the temperature of maximum action is about 40°, and it is therefore different from invertin and from maize glucase, which act most readily at 52—53° and 57—60° respectively. The enzyme becomes inactive at 55°. Up to 35°, its action is proportional to the temperature, the quantity present, and the time of action remaining constant. Increase in the quantity of enzyme does not proportionately accelerate the inversion; the addition of chloroform considerably retards the hydrolysis, only about 70 per cent. of maltose being decomposed after 24 hours. The enzyme is without action on dextrin. Full analytical details are given, and the results are tabulated and illustrated by curves. J. B. T.

Protochlorophyll. By NICOLAI A. MONTEVERDE (*Ann. Agron.*, 1895, **21**, 90; from *Acta horti. Petropolit.*, 1894, 201—217).—Etiolated leaves contain, besides xanthophyll and carotene, a colouring matter termed "protochlorophyll," which shows a red fluorescence; its absorption spectrum has a band corresponding with the chlorophyll band III, and another band at some distance from the chlorophyll band II, whilst the band I of chlorophyll is entirely wanting. The spectrum is displaced a little towards the right by alkalis. The substance in alcoholic solution is transformed by a few drops of hydrochloric or nitric acid into "protochlorophyllane." Protochlorophyll is separated as follows. The leaves are cut up, extracted with boiling water, pressed, and put into alcohol of 95°. The alcoholic solution

is precipitated with baryta, and the precipitate treated with alcoholic potash (10 per cent.). The alkaline solution of protochlorophyll thus obtained is straw coloured, with a feeble, red fluorescence.

When the alcoholic extract from etiolated wheat was exposed to sunlight, the chlorophyll band I appeared in three seconds, and the protochlorophyll spectrum gradually disappeared.

The spectrum, which Pringsheim and Tschirch considered to be characteristic of etioline, is a mixture of the spectra of slightly modified chlorophyll, protochlorophyll, carotene, and xanthophyll.

N. H. J. M.

Action of Inorganic Chlorides on Piperidine and the Fatty Amines. By C. A. August Michaelis (*Ber.*, 1895, **28**, 1012—1019). —*Thiopiperidine*, $(C_5NH_{10})_2S$, is obtained by the action of sulphur chloride, SCl_2, on piperidine; it crystallises in long prisms, which melt at 74°, and have a characteristic odour. It is not attacked by dilute alkalis, but dissolves in dilute acids, forming a clear solution, which soon decomposes, sulphur being deposited and sulphurous anhydride evolved. The *platinochloride* is a chocolate-brown precipitate, and the *picrate* melts at 144—145°. 1-*Thionylpiperidine*, $(C_5NH_{10})_2SO$, is obtained by the action of thionyl chloride on piperidine; it crystallises in white plates, and melts at 46°. It dissolves in acids, but very rapidly decomposes. When exposed to the air, thionylpiperidine is converted into a substance, $C_5H_{11}NSO_2$, which melts at 70° and deliquesces on further exposure to the air. It can also be obtained by passing a current of sulphurous anhydride into a solution of piperidine in dry ether. *Thiodiethylamine* is an almost colourless liquid, which boils at 84—86° (15 mm. pressure), and resembles monothiopiperidine in its other properties. *Thionyldiethylamine* is a light yellow oil, which boils at 118° (27—28 mm. pressure), and also resembles the corresponding piperidine derivative.

Tripiperidinephosphinoxide, $(C_5H_{10}N)_3PO$, is obtained by the action of phosphorus oxychloride on piperidine, and forms large plates which melt at 75—76°. It dissolves in strong hydrochloric acid, and is not decomposed when this solution is heated. It does not form either a nitroso-derivative or an acetyl derivative. The *hydrochloride* crystallises in slender needles, and the *platinochloride* melts at 215°.

A. H.

Derivatives of 4′-Phenylquinaldine and 4′-Phenylquinoline. By Wilhelm Koenigs and Franz Meimberg (*Ber.*, 1895, **28**, 1038—1046).—The *sulphate* of phenylquinoline crystallises in nacreous tablets melting at 195—196°; the *hydrochloride* melts at 96—97°, and forms double chlorides with many metallic chlorides; the *picrate* melts at 224°. The *methiodide* crystallises in long, compact, yellow needles, which melt at 222°. The *platinochloride* of the *methochloride* melts and decomposes at 253°. The methochloride is converted, by treatment with a cold solution of potassium ferricyanide, into 1′ : 4′-*methylphenylquinolone*, $C_6H_4<\begin{matrix}CPh:CH\\ NMe\cdot CO\end{matrix}$, which separates from ether in serrated crystals melting at 143—144°. When a solution of 4′-phenylquinoline in fuming sulphuric acid is allowed to stand, two

isomeric *monosulphonic acids* appear to be formed, both of which contain the sulphonic acid group in the 4′-phenyl residue. *4′-Phenyltetrahydroquinoline* is produced by the action of tin and alcoholic hydrochloric acid on phenylquinoline, and crystallises in white, lustrous plates melting at 74°. The *hydrochloride* melts at 193—194°, the *sulphate* at 158°; the *platinochloride* decomposes and melts at 215°. The *acetyl* derivative crystallises in white plates and melts at 120°, and the *benzoyl compound* forms white needles melting at 147°. *Methylphenyltetrahydroquinoline* is an oil, which yields a *picrate* melting at 222—224°. The *nitrosamine* of phenyltetrahydroquinoline crystallises in flat, yellow needles, melts at 72°, and gives Liebermann's reaction. When treated with alcoholic hydrochloric acid, it is converted into the isomeric *4′-phenylparanitrosotetrahydroquinoline*, which crystallises in small, green plates, and melts and decomposes at 199·5°. This compound is converted by reduction into 4′-phenylparamidoquinoline, which crystallises from chloroform in flat, faintly-coloured needles melting at 205°. Its ethereal solution has an intense blue fluorescence. The *picrate* melts at 233—234°, and the *platinochloride* forms orange-yellow needles.

The *hydrochloride* of 4′-phenylquinaldine crystallises in long, silky needles melting at 218—220°, and forms double chlorides with many metallic chlorides. The *picrate* crystallises in flat, yellow needles, and melts at 205—206°. The *methiodide* forms broad, yellow needles decomposing and melting at 205°; the *platinochloride* of the *methochloride* melts and decomposes at 245°. *4′-Phenyltetrahydroquinaldine* crystallises in large, yellow-coloured tablets melting at 66—67°, whilst the *hydrochloride* melts at 221°. The *nitrosamine* forms small, yellowish needles melting at 97—98°.

With the object of obtaining 4′-phenylparahydroxyquinoline synthetically, the *paranisidide* of *benzoylacetone* was prepared by heating benzoylacetone with paranisidine. It crystallises in yellow needles, and melts at 107—108°. When heated with dilute or concentrated sulphuric acid, this compound is decomposed into its constituents, and does not yield the desired quinoline derivative. A. H.

3-Methoxy-4′-phenylquinaldine: New Synthesis of γ-Phenylquinaldinic acid. By WILHELM KOENIGS and GEORG JAEGLÉ (*Ber.*, 1895, **28**, 1046—1050).—*3-Methoxy-4′-phenylquinaldine* is formed when the condensation product of acetophenone and paraldehyde is heated with paranisidine, nitrobenzene, and hydrochloric acid. The free base crystallises from benzene in thick tablets melting at 76°. The *hydrochloride* melts at 205·5°, the *sulphate* at 201°, the *picrate* indefinitely at 185—190°, and the nitrate at 169—170° with decomposition. The *platinochloride* melts and decomposes at 232—234°. *3-Hydroxy-4′-phenylquinaldine* is formed when the base is boiled with hydrobromic acid. It melts at 248°, and is soluble in both acids and alkalis.

γ-Phenylquinaldinic acid can be obtained directly by heating benzoylacrylic acid with aniline, nitrobenzene, and hydrochloric acid; a yield of about 15—20 per cent. of the acid used being obtained.

A. H.

Constitution of Pyrazolones. By SIEGFRIED RUHEMANN and ROBERT S. MORELL (*Ber.*, 1895, **28**, 987—989).—In the light of Claisen and Haase's recent research (this vol., i, 193), the authors assign the formulæ $\begin{matrix}N=CH\\ |\\ NPh\cdot CO\end{matrix}>CMe\cdot COOEt$, $\begin{matrix}N=CH\\ |\\ NH\cdot CO\end{matrix}>CH\cdot COOEt$, and $\begin{matrix}N=CH\\ |\\ NH\cdot CO\end{matrix}>CH_2$ or $\begin{matrix}NH\cdot CH\\ |\\ NH\cdot CO\end{matrix}>CH$ to the ethylic methylphenylpyrazolonecarboxylate (Trans., 1892, 798), ethylic isopyrazolonecarboxylate, and isopyrazolone (Abstr., 1894, i, 476; this vol., i, 20) prepared by them. The first of these, when treated with hydrochloric acid, yields the corresponding *acid;* this is comparatively stable, and melts and decomposes at 189°. C. F. B.

Antipyrine Patents. By R. v. ROTHENBURG (*Ber.*, 1895, **28**, 1124).—A reply to Knorr (this vol., i, 396). C. F. B.

Derivatives of Orthonitrobenzylic Thiocyanate. By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1025—1029).—Orthonitrobenzylic thiocyanate is converted by ammonium sulphide into orthonitrobenzylic bisulphide, which yields *orthamidobenzylic hydrosulphide*, $NH_2\cdot C_6H_4\cdot CH_2\cdot SH$, on reduction with tin and hydrochloric acid; its *hydrochloride* melts at 170—172°. This substance is converted by the action of iodine into *orthamidobenzylic bisulphide*, which forms granular crystals, and melts at 90—91°. The *acetyl*-compound crystallises in needles, and melts at 202—205°.

Orthonitrobenzylic thiocyanate is converted by sulphuric acid in the cold into *orthonitrobenzylic carbaminthiolate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot CO\cdot NH_2,$$

which crystallises in colourless needles, and melts at 115—117°. This substance is converted by reduction into a base, which is an oily liquid, boils at 242—242·5°, and has a characteristic odour, somewhat resembling that of quinoline. The *platinochloride* forms brownish needles. This compound is isomeric with benzothiazole (methenylamidophenyl mercaptan), and is probably *benzisothiazole*, $C_6H_4<\begin{matrix}CH\\ |\\ N-\end{matrix}>S$.

A. H.

Halogenised Amines. By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1029—1038; compare Abstr., this vol., i, 190).—Thiocarbamide reacts with orthamidobenzylic chloride in a similar way to the thiamides, orthobenzylene-ψ-thiocarbamide, $C_6H_4<\begin{matrix}CH_2\cdot S\\ |\\ NH\cdot C:NH\end{matrix}$, being produced. This substance crystallises from chloroform in lustrous, white, rhombic plates, and melts at 136—137°. It is readily soluble in acids; the *platinochloride* melts at 221—223° with sudden decomposition, and the *picrate* forms yellow needles and melts at 236°. This compound, which has previously been prepared by Cassirer, who gave to it the name thiocyanorthotoluidine, is formed by the reduction of orthonitrobenzylic thiocyanate (Abstr., 1893, i, 16).

When heated with aniline, it yields a product which is identical with the benzophenyldihydrothiometadiazine prepared by Söderbaum and Widman (Abstr., 1890, 178), the constitution of which was proved by Paal and Vanvolxem (Abstr., 1894, i, 621) to be represented by the formula $C_6H_4<\begin{matrix}CH_2\cdot S\\ |\\ NH\cdot C:NPh\end{matrix}$. The same substance is formed by the action of orthamidobenzylic chloride on phenylthiocarbamide.

This view of the constitution of orthobenzylene-ψ-thiocarbamide is borne out by the behaviour of the substance towards oxidising agents. Barium permanganate converts it into the barium salt of an acid substance, the *silver* salt of which has the formula $C_8H_5N_2O_3SAg$, and is a colourless microcrystalline powder. This silver salt is decomposed by hydrochloric acid with evolution of sulphurous anhydride, and formation of a base, the *hydrochloride* of which crystallises in lemon-yellow, vitreous prisms. The free *base*, $C_6H_4<\begin{matrix}CH:N\\ |\\ NH\cdot CO\end{matrix}$, is an almost white, amorphous mass, and is identical with the quinazolone produced by the condensation of orthamidobenzaldehyde with carbamide.

When the silver salt of the oxidation product of orthobenzylene-ψ-thiocarbamide is treated with silver iodide, methylation, accompanied by elimination of sulphurous anhydride, takes place. The compound produced crystallises in well-developed prisms, melts at 180°, and forms crystalline salts with acids. It is probably a *benzaldehydomethylcarbamide*, but the position of the methyl group has not yet been determined with certainty. A. H.

Existence of Coniine in "Sambucus Nigra." By G. de Sanctis (*Gazzetta*, 1895, **25**, i, 49—53).—The dilute sulphuric acid extract of the stems and leaves of the common elder (*Sambucus nigra*) contains coniine. The alkaloïd was identified by analyses of its salts, and to its presence in the elder is doubtless to be traced the effect which a decoction of the leaves and stems of this tree has on the nervous system. W. J. P.

Constitution of Nicotine. By Vincenzo Oliveri (*Gazzetta*, 1895, **25**, i, 59—77).—On oxidising nicotine in potassium carbonate solution with potassium permanganate, on the water bath, nicotinic, carbonic, oxalic, and acetic acids are formed, together with free nitrogen, and possibly β-hydroxypropionic acid. With the exception of the acid last mentioned, the same products are obtained on oxidising nicotinedibenzylammonium chloride with alkaline permanganate. By the action of acetic chloride on nicotine, a mixture of the alkaloïd and its acetyl derivative seems to be obtained.

With bromine, nicotine hydrobromide forms a *perbromide*,

$$C_{10}H_{14}N_2,HBr,HBr_3,$$

which crystallises in beautiful red needles; it is converted into nicotine by ammonia, and into monobromonicotine by warm dilute

potash. If the hydrobromide is treated with excess of bromine, a *perbromide* of dibromonicotine hydrobromide, $C_{10}H_{14}Br_2N_2,HBr,HBr_3$, is formed; it is a red, viscous mass, which is converted by alcoholic potash into a resin containing a small proportion of dibromonicotine.

On adding iodine solution to nicotine hydriodide, a reddish precipitate separates, which decomposes at 200° with evolution of iodine and methylic iodide, and on distillation with potash yields methylamine. Methylamine and a small proportion of nicotinic acid are obtained on heating nicotine at 250—280° in a closed tube for 24 hours.

The dipiperidyl, $C_{10}H_{20}N_2$, obtained by Leibrecht by reducing nicotine with sodium ethoxide, is readily prepared by reducing the base with sodium amyloxide; it contains two imido-groups, and yields an oily *dinitroso*-derivative with potassium nitrite; an oily *dibenzoyl* derivative can also be prepared, together with a viscous *dicarbamide*, $C_{10}H_{20}(N{\cdot}CO{\cdot}NH_2)_2$, the *platinochloride* of which forms an amorphous yellow powder, melting and decomposing at 171°.

The author considers that none of the constitutional formulæ hitherto suggested for nicotine satisfactorily explain the various reactions of the alkaloïd, and believes that the constitution

$$C_5NH_4{\cdot}CPr{:}NMe,$$

which he now proposes, is the most probable one. W. J. P.

Methylxanthine, a Product of the Metabolism of Theobromine and Caffeïne. By Stanislas Bondzynski and Rudolf Gottlieb (*Ber.*, 1895, **28**, 1113—1118).—When rabbits, dogs, or men are dosed with theobromine or with caffeïne, *monomethylxanthine*, $C_6H_6N_4O_2$, appears in the urine. This substance can be obtained crystalline; it melts and decomposes at about 310°, dissolves in 1592 parts of water at 18° and in 109 parts when boiling; in 7575 of absolute alcohol at 17° and in 2250 at the boiling temperature. It yields *silver*, *barium*, and *sodium derivatives*, the last with $4H_2O$, one atom of hydrogen in its molecule having been replaced, apparently, by metal. C. F. B.

Quinine Hydrochloro-sulphate. By Charles Lepierre (*Bull. Soc. Chim.*, 1894, [3], **11**, 1138—1139).—The author confirms Grimaux's results (Abstr., 1893, i, 115). Quinine hydrochlorosulphate is homogeneous, and forms crystals several cm. long; it is exceedingly soluble, and the solution is stable, with the exception that, like solutions of all quinine salts, it slowly absorbs oxygen from the air. On account of its great solubility, the salt affords an excellent means of hypodermically injecting large doses of quinine.

Jn. W.

Constitution of Cinchonine. By Wilhelm v. Miller and Georg Rhode (*Ber.*, 1895, **28**, 1056—1077).—The oily compound previously obtained by the action of dilute acetic acid on cinchonine (Abstr., 1894, i, 432), is termed *cinchotoxine*, $C_{19}H_{22}N_2O$; it crystallises slowly below 0° in absence of moisture, and melts at 58—59°. It is a strong base, and liberates ammonia from its salts. The *oxalate* is identical in appearance with cinchonine oxalate. The *hydrogen*

tartrate crystallises in colourless concentric needles. The *picrate* and the salts of mineral acids crystallise with difficulty on account of their solubility; various crystalline double salts with zinc chloride, platinum chloride, and mercuric chloride have also been prepared. The only difference between methylcinchonine and methylcinchotoxine is in crystalline habit; they are believed to have the same constitution, and both yield identical derivatives. In physiological properties cinchotoxine and methylcinchotoxine resemble digitoxine, and have no antipyretic action; this characteristic property of cinchonine appears to be caused by the presence in it of a carbon-nitrogen linking, which is resolved in the preparation of cinchotoxine.

Pasteur's cinchonicine, prepared by fusing cinchonine bisulphate, has been obtained in crystals, and is probably identical with cinchotoxine, the only difference yet observed is in crystalline form. *Cinchotoxine phenylhydrazone*, $C_{25}H_{18}N_4$, is crystalline, and melts at 148°.

By the action of nitrous acid on cinchotoxine two compounds are formed, which are separated by treatment with soda; the insoluble substance is the *nitroso-derivative*, $C_{19}H_{21}N_3O_2$, which crystallises in clear, colourless prisms melting at 98°. It is feebly basic, dissolves in mineral acids, and evolves nitrous anhydride when heated with hydrogen bromide. With phenylhydrazine, it yields two *phenylhydrazones*, melting at 149° and 163° respectively, and a third compound which has not yet been examined. The lower melting hydrazone, $C_{25}H_{27}N_5O$, crystallises in concentric prisms, and forms orange-coloured salts with acids. When heated at 100°, it loses 12·19 per cent. of weight; the product is very sparingly soluble, and forms salts which resemble those of the original hydrazone. The second compound from nitrous acid and cinchotoxine has the formula $C_{19}H_{20}N_4O_3$, and crystallises in granular aggregates of colourless prisms, melting and decomposing at 198—199°; it dissolves in alkalis with a yellow colour, and evolves nitrous anhydride when heated with hydrogen bromide.

Cinchotenine reacts like cinchonine with dilute acetic acid; the product has not been isolated, but with phenylhydrazine it yields two phenylhydrazones, the one, $C_{24}H_{26}N_4O_2$, crystallises with 3 or 3·5 H_2O in long, slender needles, melts at about 286°, according to the rapidity of heating, dissolves in acids with a reddish-yellow, in alkalis with a yellow, coloration, and is reprecipitated from the latter by carbonic anhydride. The second phenylhydrazone crystallises in rhombic plates, melts at 196°, and is soluble in dilute, but not in concentrated, soda.

As a further guide to the constitution of the cinchonic compounds, the silver salts of dehydrocinchonine and dehydrocinchine were prepared; they are colourless, amorphous, give varying analytical results, and do not resemble the salts of the higher acetylenes described by Krafft and Reuter.

The molecular refraction of cinchotine dihydrochloride = 105·5, that of cinchonine dihydrochloride = 104·81; this indicates that the latter base contains a vinyl, the former an ethyl, group; the theoretical difference in molecular refraction = 0·4 and 2·1 for a vinyl group and a diagonal linking respectively. The molecular

refraction of cinchine = 89·7, that of dihydrocinchine = 88·1, indicating the presence of an acetylene linking in the latter, and of a vinyl group in the former, the calculated difference in molecular refraction = 1·77.

The constitution of cinchonine is fully discussed, and the bearing of Skraup's and Koenigs' recent investigations considered. The conversion of merochinine into γ-methyl-β-ethylpyridine renders the author's previous formula for cinchonine improbable; they propose therefore to substitute for it the following— $CMe\langle^{CH(CH:CH_2)\cdot CH_2}_{CH_2\text{———}CH_2}\rangle C(OH)(CH_2\cdot C_9NH_6)\rangle N$.

J. B. T.

Alkaloïds of Calabar Beans. By ALEX. EHRENBERG (*Chem. Centr.*, 1894, ii, 439; from *Verh. Vers. deutsch. Naturf. u. Artze.*, ii, 102).—If a salt of eserine (physostigmine) is distilled with solution of caustic alkali in a current of hydrogen, no red colouring matter is produced, but amongst the products of decomposition are methylamine and carbonic anhydride. The residual liquid contains a new base, *eseroline*, which is colourless when crystallised from absolute alcohol, but turns red by the action of moisture. If eserine is heated in a sealed tube with alcoholic ammonia at 150°, eseroline and methylcarbamide are formed, proving the probable formula of eserine to be $NHMe\cdot CO\cdot NH\cdot C_{13}H_{16}NO$. When heated with aqueous alkalis in presence of air, it first yields rubreserine, $C_{18}H_{16}N_2O_2$, which crystallises in red needles, but which is gradually converted into *eserine-blue*, which is a true dye, colouring silk and wool without mordants.

Eseridine, which accompanies eserine, is distinguished from the latter by not yielding rubreserine under the influence of alkalis and air. A third alkaloïd isolated by the author, *eseramine*, $C_{16}H_{25}N_4O_3$, crystallises from alcohol in slender, white needles. It is not identical with Harnack's calabarine, as it does not produce tetanus. The author doubts whether calabarine really exists as such in the beans.

L. DE K.

Apoquinine Derivatives. By EDUARD LIPPMANN and FRANZ FLEISSNER (*Monatsh.*, 1895, **16**, 34—44).—Apoquinine, obtained by the action of dilute hydrochloric acid on quinine (compare Hesse, *Annalen*, **205**), is really a mixture of apoquinine, apoquinine hydrochloride, and isomerides of quinine. Approximately, pure apoquinine may be obtained on recrystallising from ether the product formed by heating quinine with dilute hydriodic acid (sp. gr. 1·25—1·35). The base sinters at 160°, melts and decomposes at 210°, and yields the following salts:—A *platinochloride*, $C_{19}H_{22}N_2O_2,H_2PtCl_6$, which is a yellow, crystalline powder; an *oxalate*, $(C_{19}H_{22}N_2O_2)_2,3C_2H_2O_4$, which crystallises in needles; and an *hydriodide*, $C_{19}H_{22}N_2O_2,2HI$, which crystallises in yellow prisms. *Ethylapoquinine* is obtained on heating a mixture of apoquinine, sodium ethoxide, and alcoholic ethylic chloride in sealed tubes at 100°. It crystallises in grains and melts sharply at 182°, whereas the isomeric ethylcupreïne, or "quinethylin" of Grimaux (*Compt. rend.*, **112**, 114), softens at 160°. *Ethylapoquinine platinochloride*, $C_{19}H_{21}EtN_2O_2,H_2PtCl_6,2H_2O$, crystallises in pale yellow, flocculent masses.

G. T. M.

Organic Chemistry.

Amalgamated Aluminium as a Neutral Reducing Agent. By Hans Wislicenus and Ludwig Kaufmann (*Ber.*, 1895, **28**, 1323—1327).—Amalgamated aluminium is prepared by boiling aluminium turnings, freed from oil, with aqueous soda until a copious evolution of hydrogen has set in, rinsing once with water, and acting on the metal for 1—2 minutes with a $\frac{1}{2}$ per cent. solution of mercuric chloride; the process is then repeated, and the metal finally well washed with water, alcohol, and ether, and kept under light petroleum ready for use. The last traces of water may, after a little while, cause a reaction vigorous enough to raise the petroleum to boiling. This amalgamated aluminium decomposes water with violent evolution of hydrogen; with alcohol or ether, if these contain but slight traces of water, the same reaction occurs; the amalgam has, however, no action on the anhydrous substances. It can thus be used to reduce substances not only in solution in water or aqueous alcohol, but also when dissolved in ether or nearly absolute alcohol, if water be allowed to drop in as required. By the use of this agent exceedingly good results were obtained in the following reductions: ethylic oxalacetate to malate in ethereal solution; nitrobenzene to aniline in aqueous alcoholic solution; nitrobenzene to phenylhydroxylamine in ordinary alcoholic or ethereal solution; 1:2-nitrophenol to 1 : 2-amidophenol in ordinary alcoholic solution (compare, however, Cohen and Ormandy, *Brit. Ass. Rep.*, 1889, 550).

C. F. B.

New Class of Compounds of the Inactive Hydrocarbons. By J. Alfred Wanklyn and W. J. Cooper (*Chem. News*, 1895, **71**, 250—251).—The authors find that butyric and valeric acids form compounds, similar to the acetic acid compounds, with the hydrocarbons from Russian kerosene (this vol., i, 77) but formic acid does not.

D. A. L.

Compounds of the Sugars with Alcohols and Ketones. By Emil Fischer (*Ber.*, 1895, **28**, 1145—1167).—The method of preparing glucosides of the alcohols (Abstr., 1894, i, 3 and 565) does not yield satisfactory results with easily decomposable sugars, especially ketoses, besides which the removal of the large quantity of acid employed is, in all cases, troublesome. These difficulties may be surmounted by employing a very dilute solution of hydrogen chloride, and heating for a protracted period, under which circumstances the reaction is just as complete as when the process previously described is made use of.

When glucose is dissolved in methylic alcohol containing only 0·25 per cent. of hydrogen chloride, and the solution is heated at 100°, α- and β-methylglucoside are formed together with a third substance. The latter is most conveniently prepared by shaking anhydrous glucose with 20 parts of methylic alcohol containing 1 per cent. of hydrogen chloride for 10—12 hours, removing the hydrogen

chloride with silver carbonate, evaporating in a vacuum, and extracting with ethylic acetate. It has as yet been obtained only in the form of a colourless, sweet syrup which is very soluble in water and alcohol, but sparingly so in acetone and ethylic acetate; it remains unaltered when heated with Fehling's solution, phenylhydrazine, emulsin, yeast extract, and diastase, but is very easily reconverted into glucose by warm aqueous acids. The author regards the compound as *glucose dimethylacetal*, $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH(OMe)_2$, the analogue of the glucosemercaptals (Abstr., 1894, i, 269). If heated with alcoholic acids, it yields a mixture of α- and β-methylglucosides.

The combination of the sugars with ketones may be brought about by the new method, but attempts failed to effect the combination of the sugars with simple aldehydes on account of the tendency of the latter to polymerisation and condensation.

H. Schiff (Abstr., 1888, 572) obtained certain amorphous compounds of the sugars with aldehydes and ketones, but his views regarding their composition, structure, and properties appear doubtful to the author.

The author's formula for the glucosides,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH<\begin{matrix}(CH\cdot OH_2)\\ O\text{———}\end{matrix}>CH\cdot OR,$$

which is based on the view that these sugar derivatives behave as acetals and not as aldehydes is in best accord with the new observations. Marchlewski, however (Abstr., 1894, i, 104), brings forward arguments in support of the formula,

$$OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot CH<\begin{matrix}CH\cdot OR.\\ O\end{matrix}$$

The author maintains that Marchlewski has overlooked the fact that the conversion of glucosephenylhydrazone into the osazone is accompanied by oxidation, and that the carbinol group is only readily oxidised when it is combined with the hydrazone or aldehyde group. The formation of glucosemercaptals is an argument in favour of the aldehydic constitution of glucose, and there is no reason for assigning any other constitutional formula to this sugar now that it has been shown by Villiers and Fayolle (Abstr., 1894, ii, 489) that, when certain conditions are fulfilled, glucose colours magenta sulphurous acid. Sodium glucosate may well be an hydroxymethylene derivative, and hence its indifference towards phenylhydrazine (Marchlewski, *loc. cit.*). The author finds that, although the neutral aldehydes, as also levulinic acid and salicylaldehyde are readily converted into hydrazones in alkaline solutions, the presence of alkali prevents the formation of benzoylacetone hydrazone. The latter is obtained by treating an ethereal solution of the ketone with phenylhydrazine; it melts and decomposes at 105—110°, reduces Fehling's solution if warmed with it, and when warmed with alcoholic acids is converted into methyldiphenylpyrazole.

Methyl-d-glucosides (*loc. cit.*).—When finely pulverised anhydrous glucose (1 part) is dissolved by boiling in 4 parts of anhydrous methylic alcohol, free from acetone, and containing 0·25 per cent. of hydrogen chloride, and the solution is heated in an autoclave at 100°

for 50 hours, and subsequently evaporated to one-third of its volume, the α-methylglucoside crystallises out after some hours; a further yield of the α-derivative may be obtained by adding more methyl alcoholic hydrogen chloride to the mother liquor and heating for an additional 40 hours. If, however, it is desired to obtain β-methylglucoside, the first mother liquor is evaporated to a syrup, and placed aside for several weeks to crystallise. When starch is boiled for 15 hours with 10 parts of methylic alcohol containing 1 per cent. of hydrogen chloride, almost complete dissolution takes place, and the liquid, if treated as above described, yields a considerable quantity of α-methylglucoside. When α-ethylglucoside is heated at 100° with 10 parts of methylic alcohol containing 0·5 per cent. of hydrogen chloride, it yields a mixture of α- and β-methylglucoside, conversely α-methylglucoside may be converted into the ethyl compounds. In the preparation of the compounds which follow, the conditions have to be varied somewhat according to circumstances; in some cases it is necessary to remove the hydrogen chloride by means of silver carbonate.

Methyl-l-glucosides.—*α-Methyl-l-glucoside* prepared by the new method has the same melting point, solubility, and crystalline form as the corresponding derivative of *d*-glucose. The specific rotatory power observed was $[\alpha]_D = -156·9$. Equal amounts of the α-methylglucosides derived from *d*- and *l*-glucose form an optically inactive solution from which crystals having approximately the same melting point, 163—166°, as the optically active glucosides separate. As these crystals could not be measured, it is impossible to decide whether a true racemic compound is formed. *β-Methyl-l-glucoside* was not obtained quite pure, but the author's preparation had approximately the same melting point as the corresponding derivative of *d*-glucose.

α-Ethyl-d-glucoside crystallises in transparent prisms, melts at 113—114°, and has a specific rotatory power $[\alpha]_D = +150·5$ at 20°; it has a sweet taste, and is hydrolysed by yeast extract.

Methylgalactosides.—The α-derivative has the melting point already recorded (*loc. cit.*), but its specific rotatory power is $[\alpha]_D = +179$ at 20°. Alberda van Ekenstein has privately informed the author that he has obtained *β-methylgalactoside*. The author finds that the latter compound melts at 178—180° (corr.); it exhibits no distinct optical rotation in 10 per cent. aqueous solution. When dissolved in a cold saturated solution of borax, however, so that a concentration of 8·5 per cent. was obtained, the specific rotatory power was found to be $[\alpha]_D = +2·6$ at 20°. Unlike the α-isomeride, it is hydrolysed by emulsin. Besides α- and β-methylgalactoside, a third compound may be isolated from the mother liquor; it reduces Fehling's solution. It is under investigation.

Methylglucoheptoside, $C_7H_{13}O_7Me$, crystallises in bunches of small prisms, melts at 168—170°, has a sweet taste, and is almost insoluble in ether; its specific rotatory power is $[\alpha]_D = -74·7$ at 20°. It is not hydrolysed by yeast extract or emulsin. The isomeric compound was not isolated.

Methylxylosides, $C_5H_9O_5Me$.—The syrupy reaction product is dissolved in ethylic acetate, when the *β-compound* crystallises, after a

while, from the solution; it melts at 156—157°, tastes sweet, and its specific rotatory power is $[\alpha]_D = -65{\cdot}9$ at 20°. *α-Methylxyloside* is obtained from the ethylic acetate mother liquor; it melts at 90—92°, tastes sweet, and its specific rotatory power is $[\alpha]_D = +152{\cdot}3$ at 20°. Neither isomeride is hydrolysed by yeast extract or emulsin.

Methylrhamnoside, $C_6H_{11}O_5Me$, melts at 108—109° tastes bitter, and when heated in small amount distils unchanged. Its specific rotatory power is $[\alpha]_D = -62{\cdot}4$ at 20°.

Methylsorboside, $C_6H_{11}O_6Me$, crystallises from alcohol or acetone in transparent four-sided plates, melts at 120—122°, and its specific rotatory power is $[\alpha]_D = -88{\cdot}7$ at 20°. It is hydrolysed neither by yeast extract nor by emulsin.

Methylfructoside was obtained as an amorphous hygroscopic mass; it is reconverted into fructose (levulose) by dilute acids, and also partially hydrolysed in the same manner by yeast extract.

Methylation of Benzoylcarbinol.—When to a solution of benzoylcarbinol in methylic alcohol an amount of concentrated hydrochloric acid is added corresponding with 1 per cent. of hydrogen chloride, colourless crystals of a compound which melts at 201° (corr.) separate out. Its constitution is perhaps represented by the formula,

$$OMe{\cdot}CPh\begin{<}\begin{matrix}CH_2{\cdot}O\\O{\cdot}CH_2\end{matrix}\end{>}CPh{\cdot}OMe,$$

with which analyses and cryoscopic determinations are in accord.

Anhydrous rhamnose has hitherto been obtained only in an amorphous condition; it may, however, be crystallised from dry acetone, from which it separates in the form of needles, and then melts at 122—126°.

Acetonerhamnoside, $C_9H_{16}O_5$, crystallises in transparent prisms, melts at 90—91°, tastes bitter, and its specific rotatory power is $[\alpha]_D = +17{\cdot}5$ at 20°. It does not reduce Fehling's solution and is readily reconverted into rhamnose and acetone by dilute acids. Its constitution is perhaps expressed by the formula,

$$OH{\cdot}CHMe{\cdot}CH\begin{<}\begin{matrix}CH(OH){\cdot}CH{\cdot}O\\O\text{———}CH{\cdot}O\end{matrix}\end{>}CMe_2.$$

Arabinosediacetone, $C_{11}H_{18}O_5$, is prepared by dissolving arabinose in dry acetone containing 0·5 per cent. of hydrogen chloride, and shaking the solution for 20 hours. It crystallises in colourless needles, melts at 41·5—43°, is less soluble in warm than in cold water, is volatile with steam, and its specific rotatory power is $[a]_D = +5{\cdot}4$ at 20°. Its constitution is perhaps represented by the formula,

$$\begin{matrix}CMe_2{\cdot}O{\cdot}CH\text{—}CH{\cdot}O\\O{\cdot}CH_2\text{–}CH{\cdot}O{\cdot}CH{\cdot}O\end{matrix}\Big>CMe_2.$$

Fructosediacetone, $C_{12}H_{20}O_6$, crystallises in long, delicate, glistening needles, melts at 119—120°, tastes bitter, and its specific rotatory power is $[\alpha]_D = -161{\cdot}4$ at 20°. An isomeric *compound* was obtained on one occasion only, and this the author designates *β-fructosediacetone;* it melts at 97°, and its specific rotatory power is $[\alpha]_D = -33{\cdot}7$ at 20°.

Glucosediacetone, $C_{12}H_{20}O_6$, is prepared by shaking glucose for 6—8 hours with methylic alcohol containing 1 per cent. of hydrogen chloride, removing the hydrogen chloride, and evaporating in a vacuum, adding acetone and again evaporating to remove the methylic alcohol. The resulting syrup contains a mixture of glucoseacetal and unaltered glucose; it is then shaken with more acetone containing 0·5 per cent. of hydrogen chloride for 10 hours. It crystallises in long, colourless needles, melts at 107—108°, tastes bitter, and is readily hydrolysed by warm dilute aqueous acids. Its specific rotatory power is $[\alpha]_D = -18{\cdot}5$ at 20°.

Neither of the acetone derivatives described above is hydrolysed by yeast extract or emulsin. A. R. L.

Combination of Polyhydric Alcohols with Ketones. By Emil Fischer (*Ber.*, 1895, **28**, 1167—1170; compare Abstr., 1894, i, 395 and 438).—The methods adopted in condensing aldehydes with polyhydric alcohols (*loc. cit.*) are no longer applicable when ketones are employed; in such cases, combination is effected by means of very dilute hydrochloric acid.

Triacetonemannitol, $C_{15}H_{26}O_6$, is obtained by agitating finely powdered mannitol with dry acetone (10 parts), containing 1 per cent. of hydrogen chloride; the operation is carried out at the ordinary temperature, and is continued during 12 hours. The substance crystallises in colourless, slender prisms, and melts at 68—70°; it has a very bitter taste, and dissolves sparingly in hot water, being very readily soluble in organic solvents. When dissolved in absolute alcohol triacetonemannitol has $[\alpha]_D = +12{\cdot}5$ at 20°. Warm dilute hydrochloric acid (0·5 per cent.) quickly resolves it into its components.

Acetoneglycerol, $C_6H_{12}O_3$, is an odourless liquid, which boils at 82—83° under a pressure of 10—11 mm.; it is miscible in all proportions with water, alcohol, ether, chloroform, and benzene, but is less readily soluble in light petroleum, and is precipitated from aqueous solution by strong alkalis. The sp. gr. = 1·064 at 20°. Warm dilute mineral acids resolve acetoneglycerol into its components, and this result is also produced by benzoic chloride in presence of alkalis.

The resemblance between these compounds and those obtained from aldehydes is so close as to suggest similarity of structure; the constitution of acetoneglycerol, therefore, is probably expressed by one of the formulæ $CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH\cdot CH_2\cdot OH\end{matrix}$ and

$$CMe_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH_2\end{matrix}>CH\cdot OH.$$

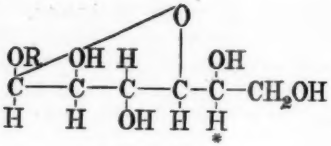
M. O. F.

Influence of Configuration on the Action of Enzymes. By Emil Fischer (*Ber.*, 1895, **28**, 1429—1438).—It has been rendered evident from the author's previous work that the hydrolysis of glucosides by the enzymes of yeast and by emulsin is dependent on molecular configuration (this vol., i, 6, 161).

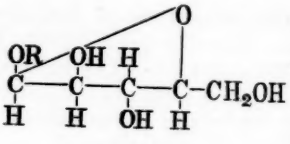
When a solution of β-methylgalactoside in water (10 parts) is heated with emulsin (0·2 part) at 33° for three days, about 35 per

cent. is converted into sugar; the behaviour of emulsin towards milk-sugar is similar, and, by analogy, the author considers the latter to be a galactoside of the β-series. Bourquelot (*Bull. Soc. Mycolog.*, 1893, **9**, 230) discovered an enzyme in *Aspergillus niger* which hydrolyses maltose, and to which he gave the name maltase. The author proposes for the future to employ the latter term in the place of the word glucase, to denote an enzyme which hydrolyses maltose.

The methyl derivatives of glucoheptose, rhamnose, arabinose, and xylose are quite indifferent towards emulsin and yeast extract. This seems at first surprising in the case of the xylosides, when the similarity of their configuration with that of the *d*-glucosides is borne in mind, thus :—



d-Glucoside.



Xyloside.

It therefore appears that the entire configuration of the *d*-glucosides is influenced by the asymmetric carbon atom marked *. The action of enzymes is limited by structure, for although glucose-ethylmercaptal and the substance which the author regards as glucosemethylacetal (this vol., i, 438) are hydrolysed by acids, they resist the action of emulsin and yeast extract. The question of structure and configuration is much more complicated in the case of the polysaccharides than in that of the glucosides: but the action of enzymes promises to be an important aid to the solution of the problem. The three enzymes—invertase, maltase, and lactase or emulsin bring about the hydrolysis of saccharose, maltose, and milk sugar respectively.

According to Bourquelot (Abstr., 1893, i, 451) invertase is without action on trehalose; the author finds, however, that when trehalose is dissolved in water (10 parts) containing thymol (0·2 part), and treated at 33° for 40 hours with dried Frohberg yeast (0·5 part), 20 per cent. of reducing sugar is formed. The diastase prepared from green malt also hydrolyses trehalose, a fact which throws some doubt on the existence of Bourquelot's trehalase from *Aspergillus niger*, since it has long been known that this mould fungus contains a diastatic enzyme, although it should be mentioned that Bourquelot states that his trehalase is rendered inactive at 64°. It seems probable that emulsin and similar substances are mixtures of different enzymes, and this has for some time been considered to be true of diastase. It is also conceivable that the same chemical molecule may be capable of various enzymic functions.

It has lately come to the author's knowledge that Bourquelot (*J. de l'Anat.*, 1886, 180 and 200) showed that maltose is hydrolysed if an aqueous solution be treated with yeast in presence of chloroform for 3—8 days, and he concluded from this that maltose is hydrolysed prior to fermentation. Lintner (*Zeit. ges. Brauw.*, 1895, 106) also

stated that maltose is hydrolysed by yeast. Morris (Proc., 1895, 46) has confirmed the author's observation as regards the action of dried or ruptured yeast cells on maltose, but finds that fresh Frohberg yeast has no action on a solution of maltose in presence of chloroform. The author now shows that the absence of action is not due to the degree of moisture, but is conditioned, to a great extent, by the chloroform; thus, little or no change is found to occur when maltose or α-methylglucoside is treated with Frohberg or Saaz yeast in presence of chloroform; considerable hydrolytic action is observed, however, in the case of both compounds when they are treated with the yeasts in presence of 0·2 per cent. of thymol or 0·3 per cent. of toluene, as also when the aqueous solutions are saturated with ether, and the vessel (test tube) in which the experiment is performed is left open so that the ether can evaporate. In the case of α-methylglucoside, the glucose produced was estimated by titration with Fehling's solution, whilst in that of maltose it was estimated as glucosazone as follows:—The liquid filtered from the yeast is heated on a water bath to precipitate the proteïds, and 10 per cent. of crystallised sodium acetate added. To the filtrate (5 c.c. of a 10 per cent. solution) pure phenylhydrazine (1 gram) and 50 per cent. acetic acid (1 gram), together with a volume of water equal to that of the total liquid are added. The mixture is now heated in a water bath for 1½ hours. The osazone, after remaining for an hour at the temperature of the room, is collected on a filter, washed with cold water, and well boiled with 50 c.c. of water; it is then filtered while hot, washed with hot water, dried at 100°, and weighed. The phenylhydrazine employed ought to dissolve to a clear solution in 2 per cent. acetic acid; it should be kept in hermetically sealed vessels. The amount of glucosazone produced being dependent on the concentration of the solution, the quantity of phenylhydrazine, and the presence of other sugars, is only an approximate method for the estimation of glucose, but qualitatively the osazone test is to be preferred to all other methods.

From these experiments, it is clear that the enzyme which hydrolyses maltose and α-methylglucoside is not formed by drying the yeast, and inasmuch as its production by the action of thymol, toluene, or ether is inconceivable, it must be concluded that it is present in normal yeast. The drying of the yeast simply permits the extraction of the enzyme by water. So long as the yeast is quite fresh and moist, hydrolysis occurs only within the cells, as the maltase, even in presence of the above-named anæsthetic agents, does not pass into solution. A. R. L.

Action of Potassium Permanganate on various Carbon Compounds. By EDME J. MAUMENÉ (*Compt. rend.*, 1895, **120**, 783—785). —Manganic oxide, prepared by the action of sugar on potassium permanganate in aqueous solution, is soluble in concentrated aqueous solutions of sugar, the solubility increasing rapidly with the proportion of sugar. The manganic oxide is gradually reduced to manganous oxide, and the sugar is oxidised to an acid. When equal weights of manganic oxide and sugar are dissolved in eight or ten times their

weight of water, and boiled for some time, the product is the acid $C_6H_{12}O_7$.

The two acids, $C_6H_{12}O_8$ and $C_3H_6O_5$, obtained by the action of permanganate on sugar, when dissolved in water in the form of potassium salts, are gradually oxidised by manganic oxide, and yield lactic and formic acids. This fact probably explains the divergence between the author's results (this Journal, 1872, 812) and those of subsequent observers. C. H. B.

Carbohydrates prepared from Formaldehyde. By TRASABURO ARAKI (*Pflüger's Archiv*, 1895, **60**, 261—262).—An answer to LOEW (this vol., i, 164). Polemical. W. D. H.

Chitosan. By TRASABURO ARAKI (*Zeit. Physiol. Chem.*, 1895, **20**, 498—510; compare Hoppe-Seyler, this vol., i, 166, 167).—Chitosan has the composition $C_{14}H_{26}N_2O_{10}$, and its formation from chitin is represented by the equation $C_{18}H_{30}N_2O_{12} + 2H_2O = C_{14}H_{26}N_2O_{10} + 2C_2H_4O_2$, as was shown by a quantitative study of the reaction, in which the chitosan was weighed as such, the acetic acid as the barium salt. When heated at 110°, chitosan decomposes, mainly according to the equation $C_{14}H_{26}N_2O_{10} + 2H_2O = 2C_6H_{13}NO_5 + C_2H_4O_2$; but secondary reactions also occur, for glucosamine and acetic acid are not the only products; some formic acid is also formed. When it is heated with acetic anhydride at 135°, it yields a derivative which resembles chitin in its properties, but contains at least three acetyl-groups—one more than that substance. It is noteworthy that the texture of the original chitin, from the carapace of the lobster, is retained in all these compounds; chitin can be converted into chitosan, this into its acetyl derivative, and this back again into chitosan, without the form of the substance, or even its microscopic structure, being altered. Chitosan is coloured violet by dilute iodine solution; its acetyl derivative and chitin are not. The author agrees with Winterstein (this vol., i, 199), that the tissues of fungi contain a substance very closely allied to chitin. C. F. B.

Hexamethylenetetramine Compounds. By MARCEL DELÉPINE (*Compt. rend.*, 1895, **120**, 743—745).—The compound, $C_6H_{12}N_4,2HgCl_2 + H_2O$, is obtained in silky needles by mixing cold aqueous solutions of its proximate constituents; whilst in hydrochloric acid solutions, $C_6H_{12}N_4,HCl,2HgCl_2 + H_2O$ is also obtained in silky needles. The former melts at about 208°, and the latter at 165°, and both combine with two atomic proportions of bromine.

The compound, $C_6H_{12}N_4,2HgCl_2 + NH_4Cl,2HgCl_2 + 3H_2O$, is found in concentrated solutions in presence of ammonium chloride, and forms hard, transparent, prismatic crystals which combine with two atoms of bromine for each molecule of the amine.

All these compounds, when boiled with water, yield yellow mercuric oxide, ammonium chloride, and formaldehyde.

With phenylhydrazine hydrochloride, hexamethylenetetramine yields the crystalline compound, $C_{15}H_{16}N_4$, obtained by Wellington and Tollens from phenylhydrazine and formaldehyde (Abstr., 1886,

330); and since ammonia is present in the mother liquor, it seems probable that the hexamethylenetetramine first splits up into ammonia and formaldehyde. The formation of the compound is, however, much less rapid than with formaldehyde alone. C. H. B.

Methylnitramine. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1894, **13**, 308—330).—Methylnitramine is reduced by zinc dust to methylic alcohol and nitrogen. As no methylhydrazine is formed, and as the amount of zinc used is much less than that required to form the latter, it is probable that methylamine and nitrous acid are the first products, and that the alcohol and nitrogen are due to their mutual action; small quantities of these intermediate products can, in fact, be detected. With sodium amalgam in alkaline solution, the main action is the same, but some hydroxylamine is probably also formed.

The acid properties of methylnitramine are rather stronger than those of carbonic acid, as it displaces the latter from its salts. The *ammonium*, *silver*, *zinc*, *cadmium*, *mercury*, and *copper* salts are crystalline; the *barium* salt crystallises with 1 mol. H_2O; the *lithium*, *calcium*, and *magnesium* salts could not be crystallised. The copper and zinc salts are decomposed by water into *basic* salts and the free nitramine, in this resembling the carbonates; but the silver and mercuric salts are quite stable.

The alkylic salts are prepared by acting on an alcoholic potash solution of the potassium salt with the alkylic bromide in closed vessels at 100°. *Methylethylnitramine*, $NMeEt{\cdot}NO_2$, the molecular weight of which was determined by the vapour-density method, melts at −30° and boils at 195·7°; sp. gr. = 1·100 at 15°; it is insoluble in water, and, in accordance with van Erp's rule, is hydrolysed by caustic alkalis into ethylamine and formic and nitrous acids. *Methylpropylnitramine* boils at 115—116° (40 mm.), or at 208—210° (atmos.), in the latter case decomposing partially; sp. gr. = 1·063 at 15°. *Methylisopropylnitramine* boils at 60—61° (40 mm.). JN. W.

Action of Nitric Peroxide on Ketoximes. By ROLAND SCHOLL and GEORG BORN (*Ber.*, 1895, **28**, 1361—1368; compare Abstr., 1888, 443).—When pinacolinoxime, $CMe_3{\cdot}CMe{:}NOH$, is treated in ethereal solution with nitric peroxide, *pinacolinenitrimine*, $CMe_3{\cdot}CMe{:}N{\cdot}NO_2$, is formed as a colourless oil which boils at 81—83° (at 10 mm. pressure). This substance has not the characteristic properties of a nitroso-compound, and is not altered by boiling with sodium ethoxide in alcoholic solution, so that the formula given is most probably correct. When it is treated with hydroxylamine hydrochloride, it is reconverted into pinacolinoxime. Oxidation with chromic acid and acetic acid converts the nitrimine into a white, crystalline substance of the formula $C_6H_{12}N_2O_2$, which has only been obtained in exceedingly small quantity. It melts at 172°, and is very volatile, subliming at the ordinary temperature. Its formula shows that it cannot be a dinitromethane derivative such as $CMe(NO_2)_2{\cdot}CMe_3$, and this is a further proof that the constitution of the nitrimine is not represented by the formula $CMe_3{\cdot}CMe(NO)_2$.

Acetoxime is converted by nitrogen peroxide in ethereal solution into propylpseudonitrole and a substance which is probably *tetramethyldinitroazoxymethane*, $O<\begin{matrix}NCMe_2\cdot NO_2\\|\\NCMe_2\cdot NO_2\end{matrix}$. The latter, which is only formed in small quantity, separates from ether in colourless, rhombohedral crystals, which are odourless and melt at 97°. A. H.

Aldehydes of the Acetic Series. By Louis Henry (*Compt. rend.*, 1895, **120**, 837—840).—In the aldehydes of the acetic series the group CHO is a smaller fraction of the molecule the higher the molecular weight, and it would seem to follow that the energy of the aldehydic function should diminish as the molecular weight increases. This is well seen in the tendency to polymerise, which is most marked in the case of formaldehyde, and decreases as the molecular weight increases. A similar change is observed in the energy with which the aldehydes interact with alkylamines, and in the tendency of the products, which will be described subsequently, to polymerise. The reaction between the aldehydes and the amines is also more energetic the lower the molecular weight of the amine, or in other words, the higher the ratio of the NH_2-group to the rest of the molecule. The tendency of the products (the aldehydic amines) to polymerise, also diminishes with an increase in the molecular weight of the alkylic radicle of the amine.

The boiling points of these aldehydic amines are, as a rule, almost identical with those of the corresponding dialkylamines. The elimination of a molecule of hydrogen in the system $H\dot{C}\cdot\dot{N}H$, with production of double linking between carbon and nitrogen $>C{:}N-$, has very little effect on the volatility. C. H. B.

Preparation of Thioacetic acid. By Robert Schiff (*Ber.*, 1895, **28**, 1204—1206).—See this vol., ii, 370.

Proteïn-like Substances. By Leon Lilienfeld (*Chem. Centr.*, 1894, ii, 478; from *Du Bois-Reymond's Archiv.*, 1894, 383—386).—If ethylic amidoacetate is heated with potassium hydrogen sulphate for some time on the water bath, a base, *biuretdimethylene*,

$$NH(CO\cdot NH_2{:}CH_2)_2(?),$$

is formed, the *carbonate* of which, $C_5H_9N_3O_4$, was obtained crystallised. When this is heated with water, a substance is formed which has the physical properties and percentage composition of gelatin.

Ethylic amidocaproate is a yellow liquid; ethylic hydroxyphenylamidopropionate a crystalline solid. These, and also ethylic aspartate, condense with the above-mentioned base, yielding products which exhibit the reactions of proteïds. C. F. B.

The Drying of Fats. By Ach. Livache (*Compt. rend.*, 1895, **120**, 842—845).—Non-drying oils, when treated with manganese or lead oxides or salts and exposed to the air in thin layers, do not dry even after several months' exposure. If, however, non-drying oils or fats, solid or liquid, are heated at 120—160°, either alone or in presence of

lead or manganese compounds, in such a manner as to expose a large surface to the air, drying takes place somewhat rapidly—especially if the metallic compounds are present.

The product obtained is yellow, transparent, very elastic, swells up in ether, benzene, alcohol, &c., without dissolving, and is easily saponified by alkalis. It seems, therefore, to be identical with the linoxin obtained from drying oils and fats; but this point is under investigation.

The classification of vegetable oils into drying and non-drying oils is well defined at the ordinary temperature, but at a higher temperature the distinction disappears, and all oils and fats, whether of animal or vegetable origin, yield a solid product if heated for a sufficient length of time at a suitable temperature. C. H. B.

Undecanonic acid. By E. WELANDER (*Ber.*, 1895, **28**, 1448—1450).—Undecolic acid, $C_{11}H_{18}O_2$, is best prepared by heating the dibromide of undecylenic acid with concentrated aqueous potash at 180°. *Ethylic undecolate*, $C_{11}H_{17}O_2Et$, boils at 197° (at 49 mm. pressure). *Undecanonic acid*, $COMe[CH_2]_8{\cdot}COOH$, (?) is obtained by treating undecolic acid with sulphuric acid. It crystallises from boiling water in plates which melt at 49°. The *oxime*, $C_{18}H_{20}O_2{:}NOH$, is an oil, and the *silver* salt a white precipitate. A. H.

Oxidation of Ethylic Isonitrosoacetoacetate with Nitric acid. By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 1213—1217; compare Abstr., 1892, 699).—Cramer has shown (*loc. cit.*) that the compound obtained by Pröpper from ethylic acetoacetate and nitric acid is formed by elimination of $2H_2O$ from 2 mols. of ethylic oximidoacetate, and has the constitution $\begin{matrix} O{\cdot}N{:}C{\cdot}COOEt \\ | \\ O{\cdot}N{:}C{\cdot}COOEt \end{matrix}$. The author has oxidised ethylic isonitrosoacetoacetate with nitric acid, obtaining, together with acetic acid, a compound of the formula $NO_2{\cdot}C(NOH){\cdot}COOEt$, for which the name ethylic oximidonitroacetate or ethylic acetate-nitrolic acid is suggested; this result is analogous to the formation of acetylmethylnitrolic acid on treating isonitrosoacetone with nitric acid.

Ethylic oximidonitroacetate is obtained by dissolving ethylic isonitrosoacetate in nitric acid (sp. gr. 1·2); the liquid is cooled during solution, and when the reaction is finished, treated with twice or thrice its volume of water. Ether extracts the substance, which crystallises in large prisms, and melts at 69°, decomposing at a slightly higher temperature. The compound is more stable in the atmosphere than when preserved in the desiccator, the nitrous acid which arises from its decomposition being free to escape without having further action on the substance. It is decomposed by alkalis, developing a reddish-yellow coloration, and water also attacks it; the substance dissolves very readily in ether and alcohol, but is insoluble in light petroleum. It has an irritating effect on the eyes, and attacks the skin vigorously.

The action of nitric acid on ethylic isonitrosoacetoacetate also gives rise to the compound obtained by Pröpper, to which reference has been already made, and this is separated from ethylic oximidonitroacetate

by decomposing the latter with sodium carbonate, which is without effect on the compound in question; it is also formed on heating ethylic oximidonitroacetate at 70—75°, or allowing it to remain in closed vessels for several weeks.

When ethylic oximidonitroacetate remains in contact with concentrated hydrochloric acid for 24 hours, ethylic chloroximidoacetate is formed. M. O. F.

Ethylic β-Amidoanticrotonate. By René Thomas-Mamert (*Bull. Soc. Chim.*, 1895, [3], **13**, 68—72).—To decide whether the product of the action of ammonia on ethylic acetoacetate is an amidocrotonate or an imidobutyrate, ethylic β-amidocrotonate was made from the corresponding chloro-compound. Ethylic β-chloranticrotonate is conveniently prepared by the action of phosphorus pentachloride on ethylic acetoacetate in benzene solution; after removal of the reagent and solvent, the product consists of a mixture of the two stereoisomeric salts, but the syn-compound can be converted into its isomeride by boiling with iodine. The amido-compound obtained by heating the chlorocrotonate with alcoholic ammonia at 100° yields the acetyl derivative described by Collie (Abstr., 1887, 501), and is identical in physical and chemical properties with the product of the action of ammonia on ethylic acetoacetate. The latter, therefore, is ethylic β-amidoanticrotonate. The corresponding methylic salt, prepared in a similar manner, is identical with that described by Conrad and Epstein (Abstr., 1888, 253).

Since anticrotonic (isocrotonic) acid is related to acetoacetic acid, it must be a stereoisomeride of crotonic acid, and Fittig's formula (*Annalen*, **226**, 309) $CH_2{:}CH{\cdot}CH_2{\cdot}COOH$, must be rejected.

Jn. W.

Rotatory Power of Alkylic β-Methyladipates. By P. Freundler (*Bull. Soc. Chim.*, 1895, [3], **13**, 6—10).—A further instalment of the work on the validity of Guye's formula, and on the influence of solvents on rotatory power (compare this vol., i, 173, 210, 267).

β-Methyladipic acid (γ-pimelic acid) is best prepared by oxidising menthone with neutral permanganate, and may be extracted with ether from the clear, acidified product after saturation with ammonium sulphate; the menthone is conveniently prepared from menthol by oxidation with chromic acid. The pure acid crystallises in colourless plates, and melts at 91—92°, not at 89·5°, as stated by Manasse and Rupe (Abstr., 1894, i, 470); it boils undecomposed at 211° under 21 mm. pressure, but under ordinary pressure is partially converted into the anhydride (compare, however, the authors cited); the specific rotatory power in 2 per cent. aqueous solution is $[\alpha]_D = +8{\cdot}4°$.

The alkylic salts are readily prepared by the hydrogen chloride method. The *methylic* salt is a colourless, mobile liquid, having a faint, fruity odour, and boiling at 134—135° (40 mm.); sp. gr. = 1·008 at 18°; the specific rotatory power is $[\alpha]_D = +0{\cdot}6$. The ethylic salt (compare Semmler, Abstr., 1893, i, 130) boils at 127° (10 mm.), or at 165—170° (50 mm.); sp. gr. = 0·998 at 18°; the specific rota-

tory power of the liquid is $[\alpha]_D = -0{\cdot}9$, of the 6 per cent. benzene solution $[\alpha]_D = -1{\cdot}0°$.

The change of sign of the rotatory power in passing from the acid through the methylic salt to its higher homologue is not predicted by Guye's formula; it may be, however, that the length of the substituted chains has reached in these compounds the limiting point beyond which the free rotation required by Guye's hypothesis is no longer possible.

As regards the influence of solvents on the physical properties of the dissolved substance, the author's view that polarimetric and cryoscopic anomalies are due to a common cause, namely, a peculiar kind of dissociation (this vol., ii, 194), is completely borne out by the behaviour of ethylic β-methyladipate. The structure of the alkyladipates does not admit of the peculiar dissociation to which the acidyltartrates may be considered liable, and their polarimetric and cryoscopic properties should therefore be independent of the solvent; in the only compound of the series that has been fully examined, namely, this ethylic salt, this is the case. The author is now studying the higher homologues. JN. W.

Ketonic Compound from Tartaric acid: Parapyruvic acid. By EDUARD MULDER (*Rec. Trav. Chim.*, 1894, **13**, 345—402; compare Abstr., 1893, i, 685).—The products, respectively soluble and insoluble in acetic acid, which result from the action of ethylic chloride on ethylic disodiotartrate, have now been proved to yield acetic and oxalic acids, and a modification of pyruvic acid. The insoluble compound is probably ethylic sodiotartryltartrate, and the soluble compound, ethylic sodioethyltartryltartrate. Tartryltartaric acid can be resolved into acetic and oxalic acids, or into carbonic and glyceric acids. The pyruvic acid might readily arise from the latter by simple dehydration.

The soluble substance mentioned above seems to form a loose, colloidal compound with sodium chloride. In connection with this, it is noteworthy that barium tartrate and oxalate, when precipitated in the presence of pyruvic acid, are amorphous and gelatinous, and readily dissolve, and remain dissolved, in acetic acid, whereas, when precipitated alone, as is well known, they soon become crystalline and insoluble. These facts may prove of importance in vegetable physiology. JN. W.

Resolution of Pyrotartaric acid into its Optical Components. By ALBERT LADENBURG (*Ber.*, 1895, **28**, 1170—1171).—Pyrotartaric acid, melting at 117—118°, was converted into the strychnine salt, which melts at 186°; this yields a specimen of the acid which melts at 115°. On repeating this operation, dextro-rotatory pyrotartaric acid is isolated, whilst the lævo-modification may be obtained from the mother liquors of the strychnine salt.

M. O. F.

Amido-derivatives of Oxalic acid. By ANTOINE P. N. FRANCHIMONT and H. A. ROUFFAER (*Rec. Trav. Chim.*, 1894, **13**,

331—344).—Of the five methyloxamides, only the mono- and symmetrical di-derivatives are accurately known. Tetramethyloxamide is prepared by a method analogous to that used by Hammerich (Abstr., 1892, 1084) in preparing the corresponding tetrabenzyl compound, namely, by acting with sodium on *dimethylcarbamic chloride* in ethereal solution. This chloride is best prepared by the action of carbonic chloride on dimethylamine in benzene solution; it melts at −33°, and boils at 167—167·5° (754·7 mm.); sp. gr. = 1·174 at 15°. *Tetramethyloxamide*, $NMe_2{\cdot}CO{\cdot}CO{\cdot}NMe_2$, crystallises in long, white needles, and melts at 80°; it is sparingly soluble in ether, but freely in chloroform and benzene, and is not appreciably attacked by nitric acid; it is hydrolysed by baryta water into *barium dimethyloxamate*, which is very soluble in water; the free *acid* crystallises from chloroform and benzene in long, flat needles or prisms, and melts at 130°, decomposing at a higher temperature into carbonic anhydride and *dimethylformamide*, $H{\cdot}CO{\cdot}NMe_2$. This is a colourless liquid, which boils at 153° (corr.), and remains liquid even at − 55°; sp. gr. = 0·9525 at 15°.

Dimethyloxamamide, (unsymmetrical dimethyloxamide),

$$NMe_2{\cdot}CO{\cdot}CO{\cdot}NH_2,$$

prepared from ethylic dimethyloxamate in the usual way by the action of ammonia, crystallises from benzene in small, square plates, and melts at 104°; it can be distilled unchanged under very low pressure, and is converted by nitric acid into nitrous oxide, carbonic oxide and anhydride, and dimethylamine. Ethylic oxalate melts at −41°; it is converted by aqueous dimethylamine into *dimethylammonium oxalate*, but by the dry amine into ethylic dimethyloxamate; the latter melts at −22°, and boils at 241—242°, or at 129·5° (18 mm.); sp. gr. = 1·081 at 15°.

Trimethyloxamide is obtained from this by the action of methylamine, and is separated from the solid symmetrical dimethyloxamide, which is formed at the same time (apparently by direct replacement of a dimethylamido- by a methylamido-group), partly mechanically, and partly by fractionation under low pressure; it crystallises in oblique rhombic plates, and is extremely hygroscopic; it melts at about 32°, and boils at 139° (22 mm.). Jn. W.

Optically Active Halogen Derivatives. By Paul Walden (*Ber.*, 1895, **28**, 1287—1297; compare Abstr., 1893, i, 250).—d-*Chlorosuccinic chloride*, $COCl{\cdot}CHCl{\cdot}CH_2{\cdot}COCl$, boils at 91—93° (11 mm. pressure), and has the specific rotation $[\alpha]_D = +29{\cdot}53°$. d-*Chlorosuccinic anhydride* may be prepared by shaking the acid with phosphoric anhydride and distilling in a vacuum. It melts at 80°, and has the rotation $[\alpha]_D = +30{\cdot}85°$ in solution in ethylic acetate. *Dimethylic* d-*chlorosuccinate* is obtained by the action of phosphorus pentachloride on dimethylic malate in chloroform solution. It boils at 107° (15 mm. pressure), and has the rotation $[\alpha]_D = +41{\cdot}40°$. *Diethylic* d-*chlorosuccinate* may be obtained by the etherification of chlorosuccinic acid with alcohol and hydrogen chloride. It boils at 131° (18 mm. pressure), and has the rotation $[\alpha]_D = +27{\cdot}50°$.

The action of phosphorus pentabromide on free malic acid is very slow and incomplete, whilst it acts very readily on the ethereal salts. *Dimethylic* d-*bromosuccinate* boils at 129° (23 mm. pressure), and has the rotation $[\alpha]_D = +50{\cdot}83°$. *Diethylic* d-*bromosuccinate* boils at 143° (28—30 mm. pressure), and has the rotation $[\alpha]_D = +40{\cdot}96°$.

Ethylic l-*chloromalate* is obtained by the action of phosphorus pentachloride on ethylic d-tartrate. It boils at 162—165° (15 mm. pressure), has sp. gr. = 1·2543 (at 20°/4°), and the rotation $[\alpha]_D = -8{\cdot}05°$. The fact that this compound is lævorotatory must be taken to show that it contains two asymmetric carbon atoms, since simple partial reduction of d-tartaric acid yields d-malic acid. *Ethylic* l-*bromomalate* boils at 165—168° (12—15 mm. pressure), and has sp. gr. = 1·4330, and the rotation $[\alpha]_D = -2{\cdot}44°$.

Methylic d-*chloropropionate*, CHMeCl·COOMe, is obtained by pouring the product of the action of phosphorus pentachloride on sarcolactic acid into methylic alcohol. It boils at 132—134°, and has sp. gr. = 1·1520, and the rotation $[\alpha]_D = +19{\cdot}01°$. The corresponding inactive compound, prepared from inactive lactic acid, has the same boiling point and a density of 1·1515. *Ethylic* d-*chloropropionate* boils at 146—149°, has sp. gr. = 1·0888, and the rotation $[\alpha]_D = +12{\cdot}86°$. The corresponding inactive compound has the same boiling point, and sp. gr. = 1·0869.

Ethylic d-*bromopropionate* is formed in small amount by the action of phosphorus pentabromide on ethylic d-lactate. It boils at about 162°, and has the rotation $[\alpha]_D = +7{\cdot}18°$. The corresponding inactive salt has the same boiling point and index of refraction $n_D = 1{\cdot}447$.

d-*Phenylacetic chloride*, prepared from mandelic acid, boils at 120° (23 mm. pressure), and has the rotation $[\alpha]_D = +158°$. The *free acid* melts at 56—58°, and has the rotation $[\alpha]_D = +132{\cdot}13$ in benzene solution. *Ethylic* d-*phenylchloracetate* boils at 162° (45 mm. pressure), has sp. gr. = 1·1594, and the rotation $[\alpha]_D = +25{\cdot}19°$. *Propylic* d-*phenylchloracetate* boils at 180° (60 mm. pressure), has sp. gr. = 1·1278, and the rotation $[\alpha]_D = +23{\cdot}94°$.

d-*Phenylbromacetic bromide* boils at 145—147°, and has sp. gr. = 1·853, and the rotation $[\alpha]_D = +44{\cdot}53°$. The *acid* melts at 76—78°, whilst the inactive acid melts at 83—84°. *Ethylic* d-*phenylbromacetate* boils at 164° (20 mm. pressure), has a most violent action on the mucous membrane, and has sp. gr. = 1·3893, and rotation $[\alpha]_D = +16{\cdot}56°$. *Isobutylic* d-*phenylbromacetate* boils at 167—168° (19 mm. pressure), has sp. gr. = 1·2892, and the rotation $[\alpha]_D = +9{\cdot}77°$.

These results seem to show that the optical activity of a carbon atom depends simply on the existence of a difference between the four groups with which it is combined, whilst the nature of the groups only influences the direction and amount of the rotation produced. A. H.

Action of Boron Fluoride on Organic Compounds. By V. Gasselin (*Ann. Chim. Phys.*, 1894, [7], **3**, 5—83).—In preparing boron fluoride care must be taken that the fluor-spar used does not

contain much silica. The gas is best prepared by dissolving boric anhydride in hot concentrated sulphuric acid, cooling the solution, adding the finely powdered calcium fluoride, and heating at 125—130°. The gas then comes off very regularly and steadily.

No action could be obtained with carbonic oxide or with methane.

Cold methylic alcohol absorbs exactly one molecular proportion of boron fluoride, and forms *boron methoxydifluoride*, $BF_2{\cdot}OMe$. This compound crystallises in prisms, melts at 41·5°, and boils at 87°. It dissolves readily in methylic and ethylic alcohols, but the solutions gradually decompose with formation of the borates. With water or alkalis, it decomposes readily, according to the equation $2BF_2{\cdot}OMe + 3H_2O = 2MeOH + B(OH)_3 + HBF_4$. Sodium is without action on this compound even at 100°. Sodium methoxide acts on it readily; if molecular proportions are employed *boron dimethoxyfluoride*, $BF(OMe)_2$, is formed. This is a colourless mobile liquid, fuming in the air, and burning with a green flame. It boils at 53°, and has sp. gr. = 1·053 at 0°. Water and alkalis decompose it in like manner to the difluorine compound. Sodium methoxide yields methylic borate, $B(OMe)_3$. As this compound is not well known, it was carefully purified and examined. It is a colourless liquid, which boils at 55—56°, has sp. gr. = 0·919 at 0°, and burns with a green flame. It decomposes rapidly in moist air or with water.

Dry methylic borate absorbs boron fluoride readily, with development of heat, and the re-formation first of $BF(OMe)_2$ and finally of $BF_2{\cdot}OMe$. The yield of these two compounds is much nearer the theoretical in this mode of formation than by the action of boron fluoride on methylic alcohol. In the latter reaction, a large part of the product passed over between 120—130°, and proved to be a *molecular compound* of boron fluoride and methylic oxide, $BF_3{,}OMe_2$. This is a colourless liquid, which fumes in air, and is decomposed by water, with evolution of methylic oxide. It boils at 126—127°, but dissociation takes place at this or a slightly higher temperature, as the vapour density (at the temperature of boiling aniline) gave 2·03 (theory 3·96). This compound is also readily formed, with development of heat, by the direct union of boron fluoride and methylic oxide. Its sp. gr. at 0° is 1·140. The product of still higher boiling point obtained in the action of boron fluoride on methylic alcohol contains an oily acid. Under a pressure of 3 mm. of mercury a fraction boiling at 92°, and of sp. gr. = 1·574 at 12° was obtained, giving figures approximately corresponding with the formula $BF_3O_2H_4$. With potash, it yielded a salt, $BF_2(OH),KF$. Excess of potash yields a mixture of potassium borofluoride, (KBF_4), potassium fluoride, and potassium borate. It is doubtful whether the compound $BF_2(OH),HF$ exists in the free state, or whether that and also the more or less similar compounds said to have been obtained by previous workers are not really only mixtures of boron fluoride, hydrofluoric and boric acids, &c.

With ethylic alcohol, boron fluoride reacts in the same way as with methylic alcohol. *Boron ethoxydifluoride*, $BF_2{\cdot}OEt$, crystallises in prisms, melts at 23° and boils at 82°. *Boron diethoxyfluoride*, $BF(OEt)_2$, boils at 78°, and has sp. gr. = 1·054 at 0°. The *molecular compound*, $BF_3{,}OEt_2$, boils at 123°. Ethylic borate,

$B(OEt)_3$, boils at 118—119°, and has sp. gr. = 0·887 at 0°, as found by Schiff and Bechi.

With ethylene no action could be obtained, and the author believes that Landolph's supposed compound was probably the compound BF_3,OEt_2, formed from impurities in the reacting substances.

Acetone absorbs boron fluoride readily, but only the same ethylic compounds described above are formed. Landolph's formulæ are incorrect. If heat is used, however, the boron fluoride acts as a dehydrating agent, and mesityl oxide, mesitylene, phorone, pentaallylene, $(C_3H_4)_5$, and other unsaturated compounds are formed.

With amylene, boron fluoride causes polymerisation to di- and triamylene, but forms no compounds. Benzene is without action on boron fluoride. Cetylic alcohol, glycol, and glycerol act on boron fluoride, but the products could not be isolated. Phenol and thymol have no action. Resorcinol absorbs boron fluoride, and is condensed to diresorcinol, $OH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}OH$, but no boron or fluorine compound is formed. Boron fluoride thus acts as a strong dehydrating agent.

Analytical Methods.—Modifications of the usual methods had to be employed. In determining the hydrogen and carbon by combustion, hydrogen fluoride passes forward, and vitiates the analysis if only copper oxide, lead chromate, or a mixture of these is used. This may be obviated by interposing in the length of mixed oxide and chromate several small plugs or screens of lead peroxide, which retain the fluorine. The combustion must be carried out at the lowest possible temperature, or the tube will be much acted on by the fluorine.

For determining the boron and fluorine in those compounds which are decomposed by water with formation of boric and hydrofluoric acids, the authors employed titration. If "orange Poissier No. 3" or Congo red is used, the indication is given as soon as all the hydrofluoric acid is neutralised, boric acid not affecting these indicators. If now "blue C4B" is used, the indication is given when, in addition to neutralising the hydrofluoric acid, the alkali has been added to the extent of *one* molecule of alkali to each $B(OH)_3$. The reaction is not quite as sharp with mixtures of hydrofluoric and boric acids as with those with hydrochloric and boric acids, but is still very serviceable. For gravimetric determinations, calcium fluoride and calcium or magnesium borate are the best compounds to employ. It is necessary to keep the solutions neutral in the precipitation of calcium fluoride, as otherwise the precipitation is not complete, and where the substance is originally present as a borofluoride, acid is liberated during the formation of the calcium fluoride. This is due to the action expressed by the following equation

$$NaBF_4 + CaCl_2 + 3H_2O = CaF_2 + 2HF + HCl + NaCl + H_3BO_3.$$

The filtrate from the fluoride is treated with ammonium oxalate to precipitate the lime, and the filtrate from this (containing all the boric acid as ammonium borate, together with ammonium chloride or nitrate and oxalate) evaporated in a platinum crucible containing a known weight of pure and ignited lime, or, preferably, magnesia.

This is then gradually heated to expel the ammonium salts, and finally strongly ignited, when the excess over the previous weight represents the boric acid.

Ditte's method of fusing a fluoborate with calcium chloride in the presence of a molecular mixture of potassium and sodium chlorides also gives very good results. In the melt, the fluorine is in the form of calcium fluoride, and the boric acid as the crystalline and insoluble calcium borate. The alkali chlorides are removed by washing, the mixed fluoride and borate weighed, the borate then dissolved out by a hot concentrated solution of ammonium nitrate, and the fluoride re-weighed. The boric acid determination is slightly too low, owing to a trace of the calcium borate being dissolved out with the alkali chlorides. L. T. T.

Molecular Change Produced in Allofurfuracrylic acid and Allocinnamylideneacetic acid by Exposure to Sunlight. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1443—1448; compare Abstr., 1894, i, 173, and this vol., i, 470).—Allofurfuracrylic acid is slowly converted into the ordinary acid when its solution in benzene is exposed to sunlight, but the change occurs after only about half an hour's exposure when a little iodine is added, although the solution containing iodine is quite unaltered in the dark. The analogous change is particularly rapid and striking in the case of allocinnamylideneacetic acid. The conversion of allocinnamic acid into its stereoisomeride is also facilitated by the addition of iodine to the solution, but still requires an exposure extending over several days. The action of the iodine is probably a purely chemical one. A. H.

Isomerides of Hexanaphthene (Cyclohexane). By F. MARKOVNIKOFF and MICHAËL KONOVALOFF (*Ber.*, 1895, **28**, 1234—1237; compare this vol., i, 271).—A fraction of Caucasian naphtha, free from aromatic compounds, boiling at 70°, and having sp. gr. = 0·710 at 15°, was nitrated and treated with potash. The portion insoluble in alkali boiled at 179—181°, and had sp. gr. = 1·0011 at 20°/0°; the results of analyses agreed with the formula $C_6H_{11}NO_2$. An *amine* was obtained on reduction, boiling at 114°, and having sp. gr. = 0·8367 at 0°/0° and 0·8197 at 20°/0°. The *hydrochloride* crystallises from hot water in small needles, and melts and decomposes at 228°; the *platinochloride* crystallises in highly refractive, orange-yellow octahedra and tetrahedra. The *aurochloride* crystallises in long, slender, orange-red needles.

Chlorine converts the hydrocarbon into a chloro-derivative of the formula $C_6H_{11}Cl$; it is probable that the nitro-compound has the constitution $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>CMe\cdot NO_2$. M. O. F.

1 . 3-Diethylhexamethylene. By NICOLAI D. ZELINSKY and W. RUDEWITSCH (*Ber.*, 1895, **28**, 1341—1344).—Crude diethylpimelic acid, prepared by the action of trimethylenic bromide on ethylic sodiocyanobutyrate, on distillation in a vacuum yields a colourless oil, which boils at 205—207°, and is probably *diethylketohexamethylene*,

$CO<^{CHEt\cdot CH_2}_{CHEt\cdot CH_2}>CH_2$. This substance is converted by reduction into the alcohol, $OH\cdot CH<^{CHEt\cdot CH_2}_{CHEt\cdot CH_2}>CH_2$, which boils at 209—211°, and partially solidifies on standing, the crystalline portion melting at 77—78°. When this alcohol is converted into the iodide, and the latter reduced by means of zinc and hydrochloric acid in alcoholic solution, the product consists of *diethylhexamethylene*,

$$CH_2<^{CHEt\cdot CH_2}_{CHEt\cdot CH_2}>CH_2,$$

which is a colourless liquid with an odour resembling that of petroleum. It boils at 169—171°, and has sp. gr. = 0·7957 at 22°/0°, and the refractive index 1·4388 at 20°, whence the molecular refraction is found to be 46·13. This agrees with the calculated number for a saturated hydrocarbon of the same formula, and the saturated character of the compound is also shown by the fact that it is immediately coloured by bromine vapour. A. H.

Phenylnitromethane. By ARNOLD F. HOLLEMANN (*Rec. Trav. Chim.*, 1894, **13**, 403—410).—Phenylnitromethane, $CH_2Ph\cdot NO_2$, is formed by the action of silver nitrite on benzylic chloride, as may be proved by reducing the product with zinc dust and dilute sulphuric acid, and isolating the benzylamine thus formed as its benzoyl-derivative. (Benzylbenzamide melts at 98°, and not at 105—106°, as stated by Beckmann.) Benzylic nitrite is also formed, as benzylic alcohol is present in the reduction product.

Previous attempts to isolate the nitro-compound by distillation have failed, owing to its instability even at moderate temperatures, but it may be readily isolated by means of its insoluble sodium derivative; the crude nitro-compound, obtained by extracting the product with ether, is treated with a solution of sodium methoxide in methylic alcohol, and the sodium derivative washed with benzene, and decomposed by the calculated quantity of acetic acid; the nitro-compound is then extracted with ether and purified by distillation, first with steam, and subsequently under low pressure in an atmosphere of carbonic anhydride.

Phenylnitromethane is a pale yellow, heavy oil, having an odour resembling that of nitrobenzene. It boils at 158—160° (35 mm.), and even at that temperature decomposes slightly; when heated under ordinary pressure, it decomposes entirely at a temperature far below that at which it is stated by Gabriel (*Ber.*, **27**, 2738) to boil.

Benzeneazophenylnitromethane, $NPh{:}N\cdot CHPh\cdot NO_2$, prepared by the action of diazobenzene nitrate on the pure or crude nitro-compound for purposes of characterisation, crystallises from alcohol in vermilion plates, and melts and decomposes at 101°. It forms dark, yellowish-red solutions in alkalis, from which it is reprecipitated by acids, and it dissolves in concentrated sulphuric acid to an intensely blue solution.

Benzylic nitrite, which is the principal product in the preparation

of the nitro-compound, is a liquid, the vapour of which attacks the eyes; it boils at 136—138° (35 mm.). Jn. W.

Action of Nitrous acid on Cinnamene. By E. A. Sommer (*Ber.*, 1895, **28**, 1328—1331).—When nitrous acid is passed into an ethereal solution of cinnamene obtained from coal gas (compare Priebs, Abstr., 1885, 160), the crystals, formed in addition to phenylnitroethylene, which melt at 158°. are shown to be the α-nitrosite, $C_8H_8N_2O_3$; crystals melting at 105°, and yellow crystals, perhaps identical, but melting some at 232°, some at 215°, are also obtained. When a saturated solution of potassium nitrite is allowed to act on an acetic acid solution of cinnamene, there are obtained, besides the α-nitrosite, greenish needles, melting at 103·5°, of a compound, $C_8H_6N_3O_4$, possibly a nitro-derivative of the peroxide; yellowish crystals melting at 123°, and crystals melting at 200°. White crystals melting at 130° are obtained when strong nitric acid acts on a mixture of cinnamene, amylic nitrite, and acetic acid. C. F. B.

Halogen Derivatives of Catechol. By H. Cousin (*Compt. rend.*, 1895, **120**, 840—842).—*Trichlorocatechol*, $C_6H_3Cl_3O_2$, is obtained by the action of the calculated quantity of chlorine, dissolved in acetic acid, on a solution of catechol in a mixture of acetic acid and chloroform. It crystallises from hot, dilute acetic acid in colourless, odourless prisms, with a burning taste. The crystals melt at 104—105°, and contain 1 mol. H_2O, half of which is given off in a dry vacuum, and the resulting hydrate melts at 134—135°. Trichlorocatechol is insoluble in cold water, very soluble in alcohol, ether, acetic acid, &c., Excess of chlorine converts it into tetrachlorocatechol.

Dibromocatechol, $C_6H_4Br_2O_2$, is obtained by the action of the calculated quantity of bromine on catechol in presence of acetic acid. It crystallises from hot, dilute acetic acid in large prisms, melts at 92—93°, and is insoluble in water, but soluble in ordinary organic solvents. Excess of bromine converts it into tetrabromocatechol, and when heated with sulphuric acid at about 80°, it also yields the tetrabromo-derivative and resinous products. Chlorine converts it into the tetrachloro-compound. C. H. B.

Nitrolic acids. By Alfred Werner and Hans Buss (*Ber.*, 1895, **28**, 1280—1282).—It has been found impossible to isolate alkyl ethers of the nitrolic acids, whilst acid derivatives can readily be obtained pure. *Benzoylamylnitrolic acid*, $CH_3\cdot[CH_2]_3\cdot C(NO_2):NOBz$, is formed when an alkaline solution of amylnitrolic acid is shaken with benzoic chloride. It crystallises in prisms, melts at 83°, and is very stable. The *benzenesulphonic ether* of *ethylnitrolic acid*,

$$NO_2\cdot CMe:N\cdot O\cdot SO_2Ph,$$

may be prepared from ethylnitrolic acid by the action of benzenesulphonic chloride. It crystallises in cubes melting at 90—91°.

When ehtylnitrolic acid is treated in ethereal solution with hydrogen chloride, a white substance is formed, which melts at 141°, and

deliquesces and decomposes in the air. This compound is probably a *hydrochloride* of the formula $CMeCl{:}NOH,HCl$. A. H.

Acid Benzylamine Oxalate. By Arnold F. Holleman (*Rec. Trav. Chim.*, 1894, **13**, 411—416).—In characterising benzylamine in presence of ammonia (this vol., i, 455), the platinum method did not give satisfactory results, as the platinochloride could not be completely separated from ammonium platinochloride. The benzylamine was therefore isolated as the acid oxalate. This, when prepared from pure materials, forms large, prismatic crystals with $1H_2O$, half of which it loses at 106°, and the remainder at 150°. It melts at 175°, at the same time decomposing into dibenzyloxamide *benzylammonium benzyloxamate*, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}COONH_3{\cdot}CH_2Ph$, and *formylbenzylamine* (*benzylformamide*). The last melts at 49°, and is easily soluble in alcohol and ether.

Acid ethylamine oxalate undergoes a similar decomposition into diethyloxamide and ethylformamide. Jn. W.

Paradiamidobenzylic Sulphide. By Otto Fischer (*Ber.*, 1895, **28**, 1337—1341; compare this vol., i, 343).—*Paradinitrobenzylic sulphide* is formed by the action of alcoholic ammonium sulphide on paranitrobenzylic chloride, although the product of this reaction has been described by Strakosch (*Ber.*, **5**, 698) as paranitrobenzylic hydrosulphide. It crystallises in lustrous plates melting at 159°. On reduction with stannous chloride and hydrochloric acid, it is converted into diamidobenzylic sulphide, identical in every respect with that previously prepared from benzylic acetate. A number of condensation products of the diamidobenzylic sulphide have been prepared. The orthohydroxybenzylidene compound melts at 176—177°. The corresponding cinnamylidene compound melts at 158—159°, and not at 155°, as previously stated. The *paranitrobenzylidene compound* forms yellow needles melting at 173°. The *thiocarbamide* is a yellowish-white, crystalline powder, scarcely soluble in the usual solvents, which melts above 220°, and is insoluble in alkalis. The *phthalide* of diamidobenzylic sulphide crystallises in large, yellowish needles, and melts at 225°. *Paradibenzylic sulphide tetrazo-α-naphthol* forms small, dark red crystals, and melts and decomposes at 198°. The corresponding *β-naphthol compound* forms red plates melting at 237°, whilst the *resorcinol derivative* is a brown, crystalline powder, which melts and decomposes at 211°.

Paradiamidobenzylic sulphide gives a precipitate of silver sulphide with solutions of silver salts, and also readily loses sulphur on reduction, paratoluidine being formed. It also readily reacts with aniline at 150—160° in presence of zinc chloride, diamidodiphenylmethane being formed. A. H.

Conversion of Symmetrical Triamidophenol into 1:2:3:5-Tetrahydroxybenzene (Phentetrol). By Karl Oettinger (*Monatsh.*, 1895, **16**, 248—259).—When symmetrical triamidophenol hydrochloride, in dilute solution, is heated during four to five hours, it is decomposed into ammonium chloride and trihydroxyamidobenzene hydrochloride. During this operation, it is necessary to pass

a slow stream of hydrogen through the liquid in order to prevent oxidation. The solution is then evaporated to dryness under diminished pressure and at a low temperature, and the residue is treated with acetic anhydride in order to separate the ammonium chloride from the trihydroxyamidobenzene hydrochloride. This latter compound is converted into a mixture of its tri- and tetra-acetyl derivatives, which can be distilled under reduced pressure, and subsequently separated by repeated recrystallisation from benzene.

Tetracetyltrihydroxyamidobenzene, $C_6H_2(OAc)_3 \cdot NHAc$, forms a colourless powder which consists of minute, glistening crystals. It is sparingly soluble in water, but readily dissolves in hot alcohol and benzene, and melts at 182° (uncorr.).

The *triacetyl* derivative, $C_6H_2(OAc)_3 \cdot NH_2$, is sparingly soluble in benzene, but readily in warm water and in alcohol. It forms colourless needles, which melt at 182—184° (uncorr.). Both compounds when heated with hydrochloric acid at 100° are hydrolysed into *trihydroxyamidobenzene hydrochloride* and acetic acid. The hydrochloride forms small, colourless crystals, which are readily soluble in water and in alcohol. The aqueous solution turns brown on exposure to the air, gives a deep red coloration with ferric chloride, and a green colour with alkalis.

1 : 2 : 3 : 5-*Tetrahydroxybenzene* is obtained when the pure trihydroxyamidobenzene hydrochloride is heated with excess of water at 150—160° during eight hours. The operation is best carried out in an autoclave, in which the air has been replaced by hydrogen. The phentetrol forms colourless crystals, which melt in a vacuum at 165° (uncorr.). It is readily soluble in water, alcohol, and ethylic acetate, but is insoluble in benzene, light petroleum, and chloroform. The aqueous solution gives a light yellow precipitate with lead acetate, and a red coloration with ferric chloride. With concentrated alkali, the phentetrol gives a dirty green colour, which changes to a violet-blue on dilution.

J. J. S.

Acetyl Derivatives of Symmetrical Triamidophenol. By KARL OETTINGER (*Monatsh.*, 1895, **16**, 260—265).—Bamberger (Abstr., 1884, 309) states that when dry triamidophenol hydrochloride is heated with acetic anhydride and sodium acetate, a triacetyl derivative is obtained. The author finds that the chief product of the action of acetic anhydride on the hydrochloride is a hexacetyl derivative, together with smaller quantities of the tetra- and tri-acetyl compounds.

Hexacetyltriamidophenol, $OAc \cdot C_6H_2(NAc_2)_2 \cdot NHAc$, is readily soluble in warm water, alcohol and acetic acid. After recrystallisation from alcohol, it forms small, glistening, prismatic crystals, which melt at 184°. It is slowly decomposed by dilute alkalis, and the triacetyl compound described by Bamberger is formed.

The tetra- and tri-acetyl derivatives are best separated by fractional crystallisation from water.

Triacetyltriamidophenol, $OH \cdot C_6H_2 \cdot (NHAc)_3$, forms small, colourless crystals, which melt at 279° (uncorr.). It is readily soluble in hot water and in alcohol, sparingly in ether and benzene. It dissolves in dilute alkalis, from which it is precipitated unaltered by acetic acid.

Tetracetyltriamidophenol, $OAc\cdot C_6H_2\cdot(NHAc)_3$, forms very minute, prismatic crystals, which melt at 255° (uncorr.). It is much more readily soluble in water and alcohol than the triacetyl compound. It dissolves in dilute alkalis, but on the addition of acetic acid the triacetyl derivative of melting point 279° is thrown down.

J. J. S.

Constitution of Isodiazo-hydrates. By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 1218—1222; compare this vol., i, 274).—Evidence supporting the author's views regarding the constitution of isodiazohydrates (*loc. cit.*) is afforded by the observation that these substances are formed when hydroxylamine acts on nitroso-compounds; they are, therefore, oximes of nitroso-compounds, and thus differ structurally from the normal diazo-hydrates, which are not formed in this way. Experimental details of the conversion of nitrosobenzene, parabromonitrosobenzene, and paranitrosotoluene into isodiazobenzene, parabromisodiazobenzene, and paraisodiazotoluene respectively, are to be found in the original paper.

Parabromophenylhydroxylamine, $C_6H_4Br\cdot NH\cdot OH$ [1 : 4], crystallises in silvery, nacreous plates, and melts at 91—92°; the *nitrosamine*, obtained by the action of nitrous acid, melts at 87°.

Parabromonitrosobenzene, $C_6H_4Br\cdot NO$, is obtained by oxidising parabromophenylhydroxylamine with ferric chloride; it crystallises in colourless needles, and melts at 92—92·5°, forming a grass-green liquid. This colour also characterises the solutions of the compound, which resembles the nitroso-compounds already described in regard to odour and volatility.

When parabromonitrosobenzene is treated with hydroxylamine and β-naphthol, it yields the compound obtained from parabromodiazobenzene and β-naphthol; it crystallises in lustrous, scarlet needles, and melts at 172—173°.

M. O. F.

Asymmetrical Ethylic Phenylhydrazidoacetate and its Conversion into Triazine Derivatives. By CARL D. HARRIES (*Ber.*, 1895, **28**, 1223—1230; compare the following abstract).—When the nitroso-derivative of ethylic phenylamidoacetate is reduced, ethylic phenylhydrazidoacetate is formed; it differs completely from the isomeric substance obtained by Reissert and Kayser from ethylic chloracetate and phenylhydrazine, and as, from its mode of formation, the new compound is undoubtedly asymmetrical in structure, it follows that the isomeride must be regarded as the symmetrical compound, $NHPh\cdot NH\cdot CH_2\cdot COOEt$.

Ethylic nitrosophenylamidoacetate, $NO\cdot NPh\cdot CH_2\cdot COOEt$, is a viscous, reddish-yellow oil, obtained by the action of nitrous acid on ethylic phenylamidoacetate; it is insoluble in water and alkalis and gives Liebermann's reaction.

Asymmetrical ethylic phenylhydrazidoacetate, $NH_2\cdot NPh\cdot CH_2\cdot COOEt$, is obtained by reducing the alcoholic solution of the foregoing compound with zinc dust and glacial acetic acid; it is a slightly coloured oil, which boils at 157—161°, under a pressure of 7 mm. It reduces platinum tetrachloride and silver nitrate in the cold, and Fehling's

solution when gently heated. The *hydrochloride* crystallises in long white needles; it melts and decomposes at 195—196°. The *nitrate* melts at 143—144°, and the *sulphate* crystallises in leaflets.

Asymmetrical phenylhydrazidoacetic acid is easily prepared from the ethylic salt; it crystallises from hot alcohol in lustrous, white, six-sided tablets, and melts at 167° with evolution of gas. It reduces Fehling's solution, and dissolves in nitric acid with development of a red coloration; the *hydrochloride* crystallises in long needles.

Diethylic diphenyltetrazonediacetate, $N_2(NPh\cdot CH_2\cdot COOEt)_2$, is obtained by the oxidation of asymmetrical phenylhydrazidoacetate with mercuric oxide; it crystallises from alcohol in needles, and melts at 117°. It is indifferent towards Fehling's solution and is decomposed by fuming hydrochloric acid, gas being evolved.

Ethylic benzylidenephenylhydrazidoacetate,

$$CHPh{:}N\cdot NPh\cdot CH_2\cdot COOEt,$$

is obtained from ethylic phenylhydrazidoacetate and benzaldehyde; it crystallises from ether in white, six-sided plates, sinters at 70°, and melts at 73—74°.

The *compound*, $NHPh\cdot CS\cdot NH\cdot NPh\cdot CH_2\cdot COOEt$, is obtained from ethylic phenylhydrazidoacetate and phenylthiocarbimide; it crystallises from amylic alcohol in short prisms, and melts at 155—156°.

When ethylic phenylhydrazidoacetate is heated with formamide (1 mol.) for four hours at 130°, it is converted into *hydroxyphenyldihydrotriazine*, $NPh<\begin{matrix}CH_2\cdot C(OH)\\ N=\!=\!=C\end{matrix}>N$, which crystallises in lustrous, yellowish-green plates, and decomposes at 203—204°; it dissolves in alkalis, and is decomposed when boiled for a considerable time with aqueous potash. The compound is indifferent towards Fehling's solution, and is soluble in concentrated nitric acid with development of a brownish-red coloration.

Methylphenyltetrahydroketotriazine, $NPh<\begin{matrix}CH_2\cdot CO\\ N=CH\end{matrix}>NMe$, is obtained by methylating the foregoing compound, or by heating a mixture of methylformamide and ethylic phenylhydrazidoacetate for four hours at 135°. It crystallises in lustrous, white leaflets and melts at 179—180°.

Diphenyltetrahydroketotriazine, $NPh<\begin{matrix}CH_2\cdot CO\\ N=CH\end{matrix}>NPh$ (compare Abstr., 1894, i, 57) is formed when formanilide and ethylic phenylhydrazidoacetate in molecular proportion are heated with alcohol at 150—160°; it crystallises in long, slender, needles, and melts at 204—205°. It closely resembles Widman's compound (*loc. cit.*), with which it is isomeric. M. O. F.

Action of Ethylic Chloracetate on Phenylhydrazine. By Arnold Reissert (*Ber.*, 1895, **28**, 1230—1234; compare Reissert and Kayser, Abstr., 1891, 1054).—The wide difference in properties exhibited by asymmetrical ethylic phenylhydrazidoacetate (preceding abstract) and the product obtained from ethylic chloracetate and phenylhydrazine, has led the author to reinvestigate this substance, and it

is now found that symmetrical ethylic phenylhydrazidoacetate is the product of the reaction; a certain amount of the hydrazone of ethylic glyoxylate is also formed, arising from oxidation of the chief product.

The *phenylhydrazone* of ethylic glyoxylate, $NHPh\cdot N{:}CH\cdot COOEt$, crystallises in white needles, and melts at 129°; it is feebly basic, and is oxidised when heated for a considerable time with Fehling's solution. It is readily hydrolysed with aqueous soda, yielding the *phenylhydrazone* of glyoxylic acid, which separates from ethylic acetate in yellowish crystals and melts at 138°.

Symmetrical phenylhydrazidoacetic acid has been described by Elbers (Abstr., 1885, 535). The *ethylic* salt, $NHPh\cdot NH\cdot CH_2\cdot COOEt$, is a yellow oil which solidifies at a low temperature and reduces Fehling's solution; the *hydrochloride* crystallises in snow-white needles and melts at 190—191°. M. O. F.

Benzyl Ethers of Oximes. By Alfred Werner and Hans Buss (*Ber.*, 1895, **28**, 1278—1280).—When the α-benzyl ether of benzaldoxime is heated with hydrochloric acid, only a very small amount of α-benzylhydroxylamine is produced. The chief product of the reaction is a solid substance, which crystallises from alcohol in slender needles, melts at 29°, and is probably a benzyl-ether of benzaldoxime, $CHPh{:}N\cdot O\cdot CH_2Ph$.

When acetoxime is treated in alcoholic solution with sodium ethoxide and benzylic chloride, the nitrogen ether, $CMe_2{<}\overset{O}{\underset{N\cdot CH_2Ph}{|}}$, (Beckmann, Abstr., 1889, 607), is formed in addition to the oxygen-ether which is the chief product. This substance is also formed when acetoxime is converted into the benzyl derivative by the method of Japp and Klingemann (Beckmann, Abstr., 1889, 607). A. H.

Modification of the Baumann-Schotten Method. By Albert Deninger *Ber.*, 1895, **28**, 1322).—The substance is dissolved in pyridine, the acid chloride slowly added, and the whole then poured into water. In this way *diphenylthiocarbamide* yielded a yellowish *monacetyl* and a yellow *dibenzoyl derivative*; these melt respectively at 91° and 160·5°. C. F. B.

Benzylic Chloride as a Desulphurising Agent. Derivatives of Cyanamide. By Emil Fromm (*Ber.*, 1895, **28**, 1302—1308).—Benzylic chloride in presence of alkali very readily yields substituted benzylic derivatives with sulphur compounds, such as the keturet of phenyldithiobiuret, $NPh{:}C(SH)\cdot N{<}\overset{C\cdot SH}{\underset{CMe_2}{|}}{>}N$, (Abstr., 1893, i, 575). When, however, phenyldithiobiuret itself is treated with benzylic chloride and an alkali, a further action goes on, *phenyl-ψ-benzylcyanothiocarbamide*, $NPh{:}C(SC_7H_7)\cdot NH\cdot C{:}N$, which melts at 190°, being formed, along with benzylic sulphide. It is probable that in this reaction sodium sulphide is first produced and then reacts with the benzylic chloride, the sulphur being removed from the solution in the form of insoluble benzylic sulphide. The phenylbenzyl-

cyanothiocarbamide when boiled with hydrochloric acid yields aniline and *benzylic thioallophanate*, which melts at 179—180°. The latter is decomposed by ammonia with formation of benzylic hydrosulphide and biuret.

A similar reaction occurs when phenylthiocarbamide is treated with alcoholic soda and benzylic chloride, the whole of the sulphur being removed in the form of benzylic sulphide and phenylcyanamide formed. *Benzoylphenylcyanamide* crystallises from alcohol in needles and melts at 118°. Diphenylthiocarbamide is desulphurised in the same manner, but the insoluble carbodiphenylimide which is first formed readily takes up the elements of water forming diphenylcarbamide.

Methylphenyldithio-c-methylalduret (this vol., i, 418), which is obtained by the action of acetaldehyde on methylphenyldithiobiuret, also undergoes partial desulphurisation in the presence of alcoholic soda and benzylic chloride, *methylphenylcyanothiocarbamide*,

$$NMePh\cdot CS\cdot NH\cdot C{:}N,$$

being produced. This substance crystallises in needles, melts at 210°, and is insoluble in alkalis. A. H.

Constitution of the Safranines. By Rudolf Nietzki (*Ber.*, 1895, **28**, 1354—1357).—The conclusion that the safranines have a symmetrical constitution which has been arrived at by Jaubert (this vol., i, 278) is not justified, because a substance of asymmetrical formula might just as easily be obtained by the oxidation of the mixture of metamidodiphenylamines with paradiamines. In order to decide the question, the author attempted to prepare a safranine by oxidising a mixture of diamidodurene, the constitution of which only admits of the formation of an asymmetric derivative, with metamidoditoylamine. A colouring matter is formed by the reaction which, however, is not a true safranine but a safraninone and has the formula,

$$NH<\begin{matrix}C_6H_3Me\text{———}\\C_6H_2Me(NH_2)\end{matrix}>N\cdot C_6Me_4O$$

[NH : Me : N = 1 : 4 : 6; NH : NH_2 : Me : N = 1 : 3 : 4 : 6; N : O = 1 : 4]. The *nitrate*, which is only slightly soluble in water, has the formula, $C_{24}H_{25}N_3O$, $HNO_3 + \frac{1}{2}H_2O$. The existence of an asymmetrical compound so closely related to the safranines renders it at least possible that the compounds of the latter class may also have the asymmetrical constitution. The nature of the colouring matter obtained is being further investigated. The author has found that the compound prepared from dimethylparaphenylenediamine and aniline is different from that obtained from paraphenylenediamine and dimethylaniline. The latter product, however, appears to be a monomethylsafranine, although prepared by the aid of pure dimethylaniline.

The reaction is therefore being again examined. A. H.

Thiophosphazo-compounds. By C. A. August Michaelis and W. Kärsten (*Ber.*, 1895, **28**, 1237—1246).—The action of phosphorus thiochloride on aromatic hydrochlorides is different to that of phosphorus oxychloride; compounds of the general formula RN:PSCl

are formed corresponding with phosphazobenzene chloride, PhN:PCl, prepared from phosphorus trichloride and aniline hydrochloride; no derivatives similar to the *n*-oxychlorophosphines could be isolated.

Thiophosphazobenzene chloride, NPh:PSCl, prepared by the prolonged heating of aniline hydrochloride and phosphorus thiochloride, is deposited in large, colourless, monoclinic crystals containing $\frac{1}{2}$ mol. benzene; when dry it melts at 149°, boils at 280—290° (80 mm.), and is stable towards water, alkalis, and acids. By heating with concentrated hydrochloric acid at 150°, it is resolved into aniline hydrochloride, hydrogen sulphide, and phosphoric acid. The *ethoxy*-derivative, NPh:PS·OEt, formed by the action of sodium ethoxide on the preceding compound, is deposited in colourless crystals, melts at 206°, and is extremely stable. The *anilide*, NPh:PS·NHPh, is obtained by heating phosphorus thiochloride (2 mols.) and aniline hydrochloride (1 mol.) at 130—140°, and also by the action of aniline on the above chloride; it crystallises in slender, colourless needles, melts at 226—227°, and is decomposed by prolonged boiling with soda.

Thiophosphazoparachlorobenzene chloride, $C_6H_4Cl·N:PSCl$, prepared in a similar manner to the benzene-derivative, is deposited in colourless, compact, monoclinic crystals, melts at 188°, boils at 230° (16 mm.), and is extremely stable. The *ethoxy*-derivative, $C_6H_4Cl·N:PS·OEt$, is deposited from alcohol in large, colourless, well developed, monoclinic crystals, melts at 91°, and is not decomposed by dilute soda.

Thiophosphazo-orthotoluene chloride, $C_6H_4Me·N:PSCl$, obtained from orthotoluidine hydrochloride and phosphorus thiochloride, is deposited from dilute benzene solutions in slender, transparent needles; from concentrated solution, in well developed, transparent, monoclinic crystals; it melts at 260°, boils at 290° (28 mm.), and is not decomposed by boiling alkalis or acids; it is resolved into toluidine hydrochloride, hydrogen sulphide, and phosphoric acid, when heated at 150° with concentrated hydrochloric acid. The yield is 65 per cent. of the theoretical. The *ethoxy*-derivative, $C_6H_4Me·N:PS·OEt$, crystallises in slender, colourless, stellate needles melting at 176°. The *phenoxy*-derivative, $C_6H_4Me·N:PS·OPh$, is colourless, crystalline, melts at 236°, and is not decomposed by heating with dilute acids or alkalis. The *paratolyloxy*-derivative, $C_6H_4Me·N:PS·OC_7H_7$, is crystalline, and melts at 247°. The *piperidide*, $C_6H_4Me·N:PS·NC_5H_{10}$, prepared from piperidine and the chloride, is colourless, pulverulent, melts at 236°, and is decomposed by soda, but not by dilute acids. The *anilide*, $C_6H_4Me·N:PS·NHPh$, melts at 162°, is colourless and pulverulent. The *orthotoluidide* resembles the anilide, and melts at 258°.

Thiophosphazoparatoluene chloride is prepared in a similar manner to the ortho-compound (see above) which it resembles; it crystallises in small, flat, monoclinic prisms, melts at 170°, and decomposes when distilled, even under reduced pressure. The *ethoxy*-derivative is deposited in colourless, feathery crystals, and melts at 176°. The *paratoluidide* is yellow, pulverulent, and melts at 182°. The *piperidide* crystallises from benzene, and melts at 275°.

Thiophosphazotrimethylbenzene chloride, $C_6H_2Me_3N:PSCl$ [Me_3 = 1 : 2 : 4], prepared from pseudocumidine hydrochloride and phos-

phorus thiochloride, crystallises in colourless needles, melts at 257°, and decomposes when distilled. The *ethoxy*-derivative is deposited in slender needles melting at 201°.

The molecular weights of the preceding compounds could not be determined on account of their sparing solubility at low temperatures; it is possible, therefore, that they are greater than the above formulæ indicate; in this case the latter would need revision, and the benzene chloride, for example, might perhaps have the formula $NPh<^{P(SCl)}_{P(SCl)}>NPh$.

J. B. T.

Addition of Hydrocyanic acid to Benzaldehyde. By CARL GLÜCKSMANN (*Chem. Centr.*, 1894, ii, 663; from *Pharm. Post*, **27**, 389).—In very dilute solution, hydrocyanic acid acts on benzaldehyde only to a very slight extent, and very slowly. C. F. B.

Piperic Aldehyde. By MAX SCHOLTZ (*Ber.*, 1895, **28**, 1368—1369).—*Piperic aldehyde*, $CH_2O_2:C_6H_3\cdot CH:CH\cdot CH:CH\cdot CHO$, is formed when piperonylacraldehyde is treated with aldehyde in alkaline alcoholic solution. It crystallises from alcohol in red plates melting at 89—90°, and, like piperic acid, gives a blood-red coloration with sulphuric acid. The *phenylhydrazone* crystallises from acetic acid in red needles, and melts at 190—192°. A. H.

Action of Chloracetone on Sodium Phenoxide and Synthesis of Cumarone Derivatives. By RICH. STOERMER (*Ber.*, 1895, **28**, 1253—1254).—*Phenoxyacetone*, $OPh\cdot CH_2\cdot COMe$, is prepared by the interaction of sodium phenoxide and chloracetone in anhydrous, phenolic solution. After purification by means of its crystalline *hydrogen sodium sulphite*, it boils at 229—230° (uncorr.), has a pleasing smell, and is a colourless oil. The *phenylhydrazone* crystallises in colourless plates with a blue fluorescence, and quickly decomposes in air. The *oxime* is oily. Methylcoumarone is formed by the action of concentrated sulphuric acid on phenoxyacetone at low temperatures. *Paratolyloxyacetone*, prepared in a similar manner to the phenoxy-derivative, is liquid, and boils at about 240°. *β-Naphthoxyacetone* melts at 85°, and yields a comparatively stable *phenylhydrazone* which melts at 154°. J. B. T.

Products of the Reduction of Oxalyldiacetophenone. By PAUL F. SCHMIDT (*Ber.*, 1895, **28**, 1206—1212).—Details of an improved method for the preparation of oxalyldiacetophenone (Brömme and Claisen, Abstr., 1888, 691) are given, by which the yield of this substance is raised from 30 per cent. to 50 per cent.; reduction is effected by suspending the finely-divided substance in benzene or ether to which 20 per cent. hydrochloric acid has been added, and agitating the liquid during the addition of small quantities of zinc dust until the ketone is completely dissolved. In this way a compound is formed which melts at 79°, and has the formula $C_{18}H_{16}O_4$; on elimination of $1H_2O$, two isomeric substances are obtained which melt respectively at 172—173° and 142°. The latter, on reduction, takes up two

atoms of hydrogen, $1H_2O$ being eliminated, and the product, $C_{18}H_{14}O_2$, melts at 119—120°.

The *compound*, $C_{18}H_{16}O_4$, which melts at 79°, is produced by the addition of 2 atoms of hydrogen to oxalyldiacetophenone, which has the constitution $COPh{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}COPh$; it is an unstable substance, and the yield obtained by the method indicated is not large. The alcoholic solution develops an intense, dark red coloration with ferric chloride, whilst cupric acetate gives rise to a *copper* salt, $(C_{18}H_{15}O_4)_2Cu$, which crystallises in slender, pale green needles and melts at 187°; the *copper* salt of oxalyldiacetophenone, on the other hand, is a greenish-yellow, amorphous substance, which has the composition $C_{18}H_{12}O_4Cu$, and does not melt below 220°.

The *dioxime anhydride*, $C_{18}H_{16}N_2O_3$, crystallises in slender, white needles and melts at 157—158°.

On decomposing the copper salt of the foregoing compound (m. p. 79°) with concentrated hydrochloric acid, or on treating the substance itself with warm alcohol or glacial acetic acid, the *compound*, $C_{18}H_{14}O_3$, is formed; this melts at 142°, and the *oxime* crystallises in white needles which melt and decompose at 185°. No coloration is developed with ferric chloride, and the substance does not form a copper salt; oxidation with nitric acid gives rise to benzoic acid. The *isomeride* is obtained by treating the original compound, $C_{18}H_{16}O_4$, with a large volume of boiling water; it crystallises from alcohol in small prisms and melts at 172—173°, whilst the *oxime* melts at 179—180°. It does not give rise to a copper salt, and no coloration is developed with ferric chloride.

Of these two isomerides, the one melting at 142° yields on reduction with hydriodic acid the *compound* $C_{18}H_{14}O_2$, which crystallises from glacial acetic acid in prisms and melts at 119—120°. It is indifferent towards cupric acetate and ferric chloride, and yields benzoic acid on oxidation with nitric acid; the oxime melts and decomposes at 192°.

When a solution of oxalyldiacetophenone in glacial acetic acid is boiled with hydriodic acid, a *compound*, $C_{18}H_{16}O_3$, is obtained which crystallises in colourless prisms and melts at 114—115°; it develops a dark red coloration with ferric chloride. The *dioxime anhydride*, $C_{18}H_{16}N_2O_2$, melts at 132°. The *dibromo*-derivative is obtained by treating the substance dissolved in carbon bisulphide with bromine, which is immediately decolorised; it crystallises from alcohol in yellowish prisms which melt and decompose at 127°. In its unsaturated character the compound melting at 114—115° differs from the foregoing substances, which do not form additive compounds with halogens; it resembles them, however, in its behaviour towards nitric acid, which gives rise to benzoic acid. From consideration of its properties, the formula $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH{:}CHPh$ appears to express its constitution. M. O. F.

Action of Amidobenzoic acid on Quinone. By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1895, **120**, 684—685).—When alcoholic solutions of orthoamidobenzoic acid and quinone are mixed,

a purple-red liquid is obtained, which after some time deposits a red-brown, crystalline precipitate of the compound

$$C_6H_2O_2(NH\cdot C_6H_4\cdot COOH)_2,$$

analogous to the products obtained under like conditions from primary amines of simple function. The two $NH\cdot C_6H_4\cdot COOH$ groups are substituted for H_2, and quinol is formed at the same time. The *quinone-bis-orthoamidobenzoic acid* is feebly soluble in alcohol, but insoluble in the other ordinary solvents. It dissolves in sulphuric acid, and forms a blood-red solution, from which it separates unchanged on addition of water. It is a feeble acid, and decomposes carbonates and dissolves readily in alkalis, but is partially precipitated from the latter solutions by a current of carbonic anhydride. When heated, it becomes pasty at about 325°, but decomposes without melting, aniline and benzoic acid being amongst the products of decomposition.

If hot solutions of quinone and orthoamidobenzoic acid in glacial acetic acid are mixed, the liquid has an intense red-brown colour, and a crystalline precipitate separates almost immediately. The mixture is heated on a water bath for about 12 hours, and the precipitate is filtered off and washed with acetic acid. The insoluble product is identical with that obtained in alcoholic solutions. The acid mother liquor, when concentrated, yields the compound

$$COOH\cdot C_6H_4\cdot N{:}C_6H_2O(NH\cdot C_6H_4\cdot COOH)_2$$

as a black compound, which melts at about 145°, and dissolves readily in alcohol. It is analogous to the compounds obtained by Zincke and Hebebrand from simple amines, and hence it follows that orthoamidobenzoic acid behaves towards quinone in the same way as simple amines, whilst the quinone has some properties in common with the diketones. C. H. B.

Etherification of Aromatic acids. By VICTOR MEYER (*Ber.*, 1895, **28**, 1254—1270; compare Abstr., 1894, i, 243, 463, and this vol., i, 93, 228).—Dibromobenzoic acid [$COOH : Br_2 = 1 : 2 : 6$] melts at 146·5°, not at 137° as previously stated. Some acids, although apparently pure, give small quantities of ethereal salts when treated in alcoholic solution with hydrogen chloride, but when the operation is repeated no salt is produced; a specimen of mesitylenecarboxylic acid gave at 0°, each time, 3·6 per cent. of ethereal salt; another specimen, after being etherified once, yielded practically none, in other respects the acids were identical; the nature of the impurity in the former specimen has not been determined. Thymotic acid, $HO\cdot C_6H_2MePr\cdot COOH$ [$COOH : OH : Pr : Me = 1 : 2 : 3 : 6$], phenylhydroxybenzoic acid [$COOH : Ph : OH = 1 : 2 : 6$], and naphtholcarboxylic acid [$COOH : OH = 1 : 2$], give no methylic salt by the action of methylic alcohol and hydrogen chloride, but the isomeric naphtholcarboxylic acid [$COOH : OH = 2 : 3$] behaves like benzoic acid. These facts show that diorthosubstituted acids are not etherified at low temperatures when one of the substituting groups is hydroxyl.

In explanation of his results, the author has previously advanced a stereochemical hypothesis, from which the following deductions may be drawn:—

1. Symmetrical trisubstituted carboxylic acids should not be etherified, but those in which the carboxyl group is linked by one or more carbon atoms to the benzene nucleus should readily yield ethereal salts. This has been already shown to be correct in the case of mesitylacetic acid and mesitylglyoxylic acid; mesitylpropionic acid could not be prepared by means of Perkin's reaction. *Tribromamidophenylpropionic acid*, $NH_2 \cdot C_6HBr_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ [$CH_2 : NH_2 = 1 : 3$; $Br_2 = 2 : 4 : 6$], is prepared from metanitrocinnamic acid; it crystallises in lustrous plates, melts at 188°, and yields 98·8 per cent. of methylic salt. *Tribromophenylpropionic acid*, $C_6H_2Br_3 \cdot CH_2 \cdot CH_2 \cdot COOH$ [$CH_2 : Br_3 = 1 : 2 : 4 : 6$], obtained from the preceding compound, crystallises in slender needles, melts at 150°, and yields about 89 per cent. of *methylic* (?) *salt*, which also crystallises in needles melting at 78°. *Trimethyl-β-benzoylpropionic acid*, $C_6H_2Me_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ [$CO : Me_3 = 1 : 2 : 4 : 6$], is prepared by the action of aluminium chloride on mesitylene and succinic anhydride in carbon bisulphide solution; it crystallises in needles, melts at 109°, and yields about 89 per cent. of ethereal salt. By the action of hydriodic acid the compound is resolved into mesitylene and succinic acid.

2. Etherification should be diversely influenced by substituting groups or elements of different relative mass. In order to test this deduction, the acids, in boiling methylic alcoholic solution, were treated with hydrogen chloride during five hours. Symmetrical trichloro-, tribromo-, and trinitro-benzoic acids and 2 : 6-dibromobenzoic acid were not etherified; thymotic acid, 2 : 6-hydroxyphenylbenzoic acid, and mesitylenecarboxylic acid gave 23·3, 76·5, and 64·5 per cent. of methylic salt respectively. Tetrachlororthamidobenzoic acid gives 22 per cent. of methylic salt when heated, but none at 0°. It appears, therefore, that those radicles which prevent etherification at high temperatures have a much greater relative mass than those which only hinder it at low temperatures, but it is probable that the methylic group and its normal homologues will produce almost identical effects, since the action is chiefly due to that carbon atom which is directly linked to the benzene nucleus.

3. According to theory, those ethereal salts which are formed with greatest difficulty should be hydrolysed least readily. The acids examined were treated in alcoholic solution with soda, during two hours at 12°. 2 : 1-Chloronaphthalenecarboxylic acid gave no acid, the isomeric acid [$COOH : Cl = 3 : 2$] gave about 71 per cent. Similar results were obtained with the corresponding hydroxy-acids.

The velocity of etherification of a number of isomeric substituted benzoic acids has also been determined. The acid (1 gram), dissolved in ethylic alcohol (10 c.c.), was mixed with saturated alcoholic solution of hydrogen chloride (90 c.c.), and treated during five hours with a slow current of hydrogen chloride, the temperature being maintained at about 20°; the quantity of ethylic salt and of unaltered acid were both determined. Figures given show the percentage of acid etherified. Toluic acids: ortho-, 26; meta-, 59; para-, 41·8.

Bromobenzoic acids: ortho-, 30·5; meta-, 69·6. Nitrobenzoic acids: ortho-, 8·3; meta, 69·9. The ortho-acids are therefore much more difficult to etherify than the isomeric compounds; this is in accordance with determinations of the velocity of hydrolysis of the two ethylic bromobenzoates, under similar conditions; 69 per cent. of the ortho- and 89 per cent. of the meta-salt is decomposed.

Tricarballylic acid and hemimellitic acid are comparable in constitution; at 0°, the former yields a tri-, the latter a di-, ethereal salt, indicating that in the first compound the open chain permits the middle carboxylic group to rotate, whilst in the second, the closed chain prevents this. J. B. T.

Condensation Products of Piperonylacraldehyde and Synthetical Piperine Derivatives. By MAX SCHOLTZ (*Ber.*, 1895, **28**, 1187—1197; compare this vol., i, 42).—*α-Methylpiperic acid*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}COOH,$$

is obtained by heating a mixture of piperonylacraldehyde with sodium propionate and propionic anhydride for six hours. It melts at 208—209°, and sublimes above this temperature. The acid is readily soluble in alcohol, ether, and acetone, and in hot glacial acetic acid, from which it separates in slender needles; it dissolves sparingly in benzene, and is insoluble in light petroleum and carbon bisulphide A deep red coloration is developed on dissolving the substance in concentrated sulphuric acid. The *sodium* salt is insoluble in alcohol, and sparingly soluble in cold water. The *barium*, *calcium*, *magnesium*, *cobalt*, *nickel*, and *copper* salts are crystalline, and scarcely soluble in water; the *silver* salt is amorphous.

α-Ethylpiperic acid crystallises from alcohol in yellow needles and melts at 179°, subliming when heated above this temperature. Its salts resemble those of methylpiperic acid.

α-Isopropylpiperic acid blackens, but does not melt, at 240°. Its salts are similar to those of the foregoing acids, whose behaviour towards solvents it resembles also.

α-Phenylpiperic acid crystallises from glacial acetic acid in needles, and melts at 208—209°. The *potassium* and *sodium* salts dissolve readily in alcohol; the *magnesium* salt is amorphous.

Piperonylenemalonic acid,* $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}C(COOH)_2$, is prepared by treating piperonylacraldehyde with acetic anhydride and sodium malonate, carbonic anhydride being eliminated; if glacial acetic acid is employed in place of the anhydride, no evolution of gas occurs. The substance crystallises from alcohol in small, brick-red needles, and melts at 205—206°. The *calcium* salt crystallises in microscopic needles, and the *silver* salt is amorphous. On heating the acid above its melting point, carbonic anhydride is evolved and piperic acid is formed. When reduced with sodium amalgam, it yields *dihydropiperonylenemalonic acid*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH(COOH)_2,$$

* The author gives the name "piperonylene" to the group $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH.$

which melts and loses carbonic anhydride at 121°. The *diethylic* salt of piperonylenemalonic acid is prepared in the usual manner from piperonylacraldehyde and ethylic malonate; it crystallises in golden-yellow leaflets, and melts at 106—107°.

Piperonylenepyruvic acid, $CH_2{:}O{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}COOH$, separates from hot water in small, reddish-yellow needles, which are brick-red when dry; it sinters at 150°, and melts at 165—167°. It dissolves sparingly in cold water, more readily, however, in alcohol and hot water; it differs from the foregoing compounds in its behaviour towards concentrated sulphuric acid, this reagent giving rise to a violet coloration.

Piperonylvinylketocarboxylic acid, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}COOH$, is obtained on heating piperonal with a mixture of pyruvic and acetic acids; it separates from hot water in the form of a yellow, microcrystalline precipitate. It sinters at 140°, and melts at 148—150°; concentrated sulphuric acid develops a blood-red coloration. The *phenylhydrazone* crystallises from alcohol in dark red needles, and melts at 155°.

Piperonyleneacetone, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COMe$, is formed on adding a few drops of aqueous alkali to a solution of piperonylacraldehyde in acetone; it crystallises in needles, and melts at 89°. The *phenylhydrazone* crystallises from alcohol in yellowish-brown needles, and melts at 141°.

Dipiperonyleneacetone, $(CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH)_2CO$, is obtained by condensing the foregoing compound with a further molecular proportion of piperonylacraldehyde. It crystallises from hot glacial acetic acid in red, stellate needles, and is orange-red when dry; it melts at 198—199°, and develops a violet coloration with concentrated sulphuric acid. The *phenylhydrazone* crystallises from alcohol in yellow needles, and melts at 58—60°.

Piperonyleneacetophenone crystallises in golden-yellow leaflets, and melts at 133°; the *phenylhydrazone* melts at 49—50°.

When piperic chloride and piperidine are brought together in benzene, piperine is formed; syntheses of homologous derivatives of piperine may be effected in a similar manner.

Methylpiperine, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CO{\cdot}C_5NH_{10}$, is obtained on adding a solution of piperidine in benzene to a mixture of methylpiperic acid and phosphorus pentachloride which has been heated on the water bath, and subsequently dissolved in benzene. It forms colourless, rhombic crystals, and melts at 125—126°. Methylpiperine is insoluble in light petroleum, but dissolves readily in other organic solvents; it is feebly basic in character, and has a peppery taste.

Ethylpiperine forms compact, colourless crystals, and melts at 118—119°; *phenylpiperine* melts at 134°.

Methylenecaffeïc piperide, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_5NH_{10}$, is prepared from methylenecaffeïc acid (Lorentz, Abstr., 1881, 48) by the method employed for the production of methylpiperine. It is very readily soluble in alcohol, from which it separates in snow-white crystals; it melts at 80°. M. O. F.

Hop Tannin and Phlobaphene. By MICHAEL M. HAYDUCK (*Bied. Centr.*, 1895, **24**, 285; from *Woch. Brauerei*, 1894, **11**, 409).—Tannin was separated from hops by Etti's method (this Journal, 1876, i, 927). It is a light brown powder, soluble in water, alcohol, and ethylic acetate. The solution gives an intense green colour, without precipitation, with ferric chloride. Phlobaphene, a red-brown powder, only very sparingly soluble in water or alcohol, gives a dirty green precipitate; it precipitates albumin. The amount of tannin in hops is best estimated by Lowenthal's method as improved by Schröder.

A solution of tannin precipitated a barley extract (previously boiled), and the precipitate redissolved on heating; phlobaphene, on the other hand, gave a precipitate which did not dissolve on heating.

Both substances act indirectly as preservatives in brewing, in removing most of the more readily decomposible matters.

N. H. J. M.

Cinnamylidenemalonic acid and the Stereoisomeric Cinnamylideneacetic acids. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1438—1443; compare Abstr., 1894, i, 173).—Cinnamylidenemalonic acid is distinctly yellow in colour, but when exposed to sunlight for two or three weeks becomes white, and at the same time much more soluble in alcohol, and is found to melt indefinitely about 30° lower than the yellow acid. No loss of weight occurs during the change, and the exact nature of the white acid has not yet been ascertained. When cinnamylidenemalonic acid is heated with an excess of quinoline at 160—170°, two monobasic acids are formed, the one described by Perkin, which melts at 165°, being accompanied by an isomeric acid melting at 138°. The latter acid forms almost the sole product when the cinnamylidenemalonic acid is heated with exactly 1 mol. of quinoline.

Allocinnamylideneacetic acid, prepared in this way, crystallises in needles melting at 138°, and is much more readily soluble in the usual solvents than the previously-known acid. The salts of the allo-acid are also much more easily soluble than those of the isomeric acid. The allo-acid is quantitatively converted into the ordinary acid when its solution in benzene is boiled with a little iodine for a short time; the same change occurs when the solution in benzene containing iodine is exposed to sunlight (compare this vol., i, 454).

A. H.

Addition of Aromatic Bases to Ethereal Salts of Benzylidenemalonic and Furfurylidenemalonic acids. By I. GOLDSTEIN (*Ber.*, 1895, **28**, 1450—1455).—*Ethylic β-anilidobenzylmalonate*, $NHPh\cdot CHPh\cdot CH(COOEt)_2$, is obtained by the direct combination of aniline with ethylic benzylidenemalonate in benzene solution. It forms colourless, silky needles melting at 98—100°. The *hydrochloride* is a white, crystalline powder.

Ethylic β-phenylhydrazidobenzylmalonate forms prisms which melt at 79—80°, and yields a crystalline *hydrochloride*. When it is heated above its melting point, it decomposes, with formation of ethylic malonate and benzylidenehydrazone. Ethylic β-phenylhydrazido-

benzylmalonate is decomposed by alcoholic potash, yielding the *potassium salt of β-phenylhydrazidobenzylmalonic acid*, which is a yellow, crystalline powder. The free acid does not appear to exist, and when a solution of the potassium salt is acidified, an immediate precipitate of benzylidenehydrazone is obtained. Ethylic β-anilidobenzylmalonate behaves in a similar manner towards alcoholic potash, the *potassium salt of β-anilidobenzylmalonic acid* being obtained in readily soluble, white needles.

Benzylidenemalonic acid itself does not form additive compounds with aromatic bases.

Ethylic β-paratoluidobenzylmalonate forms white needles melting at 80—82°. The corresponding *ortho-compound* crystallises in prisms, which melt at 67·5°.

Ethylic β-anilidofurfurylidenemalonate,

$$C_4OH_3\cdot CH(NHPh)\cdot CH(COOEt)_2,$$

crystallises in prisms, which melt at 72—73°. A. H.

Etherification of Mellitic acid and of the two Hydromellitic Acids. By J. van Loon (*Ber.*, 1895, **28**, 1270—1274).—Wöhler and Schwarz found that no ethereal salt is formed by the action of hydrogen chloride on mellitic acid in alcoholic solution. The author confirms this result, which is in agreement with Victor Meyer's rule. The two hydromellitic acids, after treatment in methylic alcoholic solution with hydrogen chloride, yielded products which, when dry, had an acid reaction; they were hydrolysed with potash, and the solution tested for methylic alcohol: in the case of hydromellitic acid with negative, in that of isohydromellitic acid with positive, results. Analysis of the silver salt showed that the isohydromellitic acid had been converted into a monomethylic derivative. These facts are also in full accordance with Victor Meyer's rule, and they suggest that in isohydromellitic acid only one carboxyl group is in the "trans" position, and that consequently a trimethylic salt might, with some difficulty, be obtained, but the attempts hitherto made have been unsuccessful. J. B. T.

Derivatives of Diphenylsulphone and of Phenylnaphthylsulphone. By Oscar Hinsberg (*Ber.*, 1895, **28**, 1315—1318; compare this vol., i, 144).—The following compounds were prepared by bringing the finely powdered quinone into excess of a cold aqueous solution of benzenesulphinic acid. *Dihydroxymethylpropyldiphenylsulphone*, $[SO_2Ph : Me : Pr : (OH)_2 = 6 : 1 : 4 : 2 : 5]$, from thymoquinone, melts at 136°. *Dihydroxyphenylnaphthylsulphone*,

$$SO_2Ph\cdot C_{10}H_5(OH)_2\ [SO_2Ph:(OH)_2 = 1 : 3 : 4],$$

from β-naphthaquinone, melts and decomposes at about 185°; its *dibenzyl derivative* melts at 178°. *Hydroxydimethylamidophenylamidophenylnaphthylsulphone*, $SO_2Ph\cdot C_{10}H_5(OH)\cdot NH\cdot C_6H_4\cdot NMe_2$, from naphthol-blue, forms greenish crystals (? colourless when pure); its yellowish *hydrochloride* decomposes at about 220°. C. F. B.

Two Isomeric Chlorides of Orthosulphobenzoic acid. By IRA REMSEN (*Amer. Chem. J.*, 1895, **17**, 309—311).—Orthosulphobenzoic chloride is found to consist of two isomeric compounds, the *symmetrical*, $COCl\cdot C_6H_4\cdot SO_2Cl$, and the *unsymmetrical*, $C_6H_4<\begin{matrix}CCl_2\\SO_2\end{matrix}>O$. The one, which is probably the symmetrical compound, forms crystals melting at 76°, and is probably identical with the chloride described by Remsen and Dohme (Abstr., 1889, 992); the other, the unsymmetrical, melts at 21·5—22·5°. Both yield the same orthosulphobenzoic acid when treated with water. With ammonia, the chloride of higher melting point yields benzoic sulphinide,

$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot NH_4,$$

whilst the unsymmetrical chloride yields ammonium orthocyanobenzenesulphonate, $CN\cdot C_6H_4\cdot SO_3\cdot NH_4$. Ammonia, water, and alkalis all act more readily on the unsymmetrical than on the symmetrical compound. With benzene and aluminium chloride, orthobenzoylbenzenesulphonic chloride, $COPh\cdot C_6H_4\cdot SO_2Cl$, is first formed, and, on continued action, orthobenzoyldiphenylsulphone, $COPh\cdot C_6H_4\cdot SO_2Ph$. This latter, when fused with potash, yields diphenylsulphone and benzoic acid. The phenols act on both chlorides, yielding coloured substances, and also the phenyl salts of orthosulphobenzoic acid. The latter reactions are being further investigated. See also three following abstracts. L. T. T.

Action of Aniline and of the Toluidines on Orthosulphobenzoic acid and its Chlorides. By IRA REMSEN and CHARLES E. COATES, jun. (*Amer. Chem. J.*, 1895, **17**, 311—330).—Several of the salts of this acid are described. *Aniline orthosulphobenzoate*,

$$NH_3Ph\cdot O\cdot CO\cdot C_6H_4\cdot SO_3\cdot NH_3Ph,$$

forms transparent, colourless needles or prisms, which melt at 165°, and begin to decompose at 185°. It is moderately soluble in boiling water, but this and other analogous salts are partially decomposed on continued boiling of the solution, some of the base being volatilised, and the *acid aniline salt* produced. The latter salt crystallises with 1 mol. aq. in needles melting at 108°. The *normal paratoluidine salt* forms thick, colourless needles, soluble in boiling water, and melting at 197°. The *acid salt* (with $1H_2O$) forms very soluble, colourless needles. The *normal metatoluidine salt* crystallises in small, granular crystals melting at 163·5°; the *acid salt* (with $\frac{1}{2}H_2O$) in large, and very soluble, rhombic crystals melting at 110°. The *normal orthotoluidine salt* forms white, easily soluble needles melting at 127·5°; and the *acid salt* (with $\frac{1}{2}H_2O$) in white needles, easily soluble in water and alcohol.

On distillation these salts are for the most part carbonised, but the paratoluidine salt, when distilled at 15 mm. pressure, yields some of the paratolil. The normal salts, when heated for some time at about 230°, give off the base in part, and form gums which may contain the unsymmetrical anil or tolil. The anils and tolils are formed by the

action of the acid chlorides on the bases. They take up water when boiled with dilute alkalis, and form the anilic and tolilic acids, which form definite salts, but lose water, and revert to the anil or tolil respectively when heated above 200°. The formation of two anilides of different physical properties, and also of two metatoluidides and probably of two paratoluidides confirms the view (see preceding abstract) that the chloride of orthosulphobenzoic acid is a mixture of two isomeric chlorides, one symmetrical and the other unsymmetrical.

With excess of aniline, orthosulphobenzoic chloride yields a mixture of two isomeric anilides. The *fusible anilide* is best obtained when the action takes place in the presence of water, and at as low a temperature as possible. It crystallises from alcohol in needles, which gradually change, when left in contact with alcohol, into large, flat prisms. Both forms of crystals melt at 196°, and are soluble in boiling alcohol. The *infusible anilide* is best formed when the reagents act on one another in the anhydrous state. It crystallises from boiling alcohol with 1 mol. alcohol in orthorhombic crystals, which lose their alcohol slowly at 130°, rapidly at 160°, turn brown at 250°, and melt and decompose to a red liquid at 270—280°. Both anilides dissolve in alkalis and alkali carbonates, and are reprecipitated by acids. Neither decompose powdered calcite when boiled therewith.

Orthosulphobenzanil, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NPh$, is usually obtained in small quantity during the formation of the infusible anilide, especially if the crude product is maintained at a moderately high temperature for some time. It crystallises in long, white, flat blades or needles, melting at 190·5°. These crystals are soluble in hot alcohol and hot ether, sparingly so in hot chloroform, and are insoluble in water and alkalis. When boiled for some time with aqueous alkalis, they yield the *anilic acid*, which forms granular crystals soluble in alcohol, alkalis, and alkali carbonates, and in much boiling water. The *barium salt* (with H_2O) crystallises in needles. *Orthosulphobenzoparatolil* crystallises in thin needles melting at 195·5°, and yields the *tolilic* acid melting at 155°. *Infusible orthosulphobenzoparatoluidide* crystallises in anhydrous, transparent cubes, which are unchanged at 250°, and decompose at higher temperatures. The *fusible paratoluidide* was only obtained in very small quantity, but apparently forms needles melting at 196°. *Orthosulphobenzometatolil* crystallises in needles or prisms melting at 147·5°. The *fusible metatoluidide* crystallises in large grains, melting at 161·5—162·5°; the *infusible metatoluiddide*, with 1 mol. alcohol, in prisms which lose alcohol at 120°, but remain solid at 250°. *Orthosulphobenzo-orthotolil* yields short, thick needles or plates, melting at 172—175°. Only one orthotoluidide was obtained, and that with difficulty, and in small quantity. It appears to be the *infusible orthotoluidide*, and to crystallise with 2 mols. alcohol. (See also preceding abstract.) L. T. T.

Action of Aniline on the Chlorides of Orthosulphobenzoic acid. By Ira Remsen and E. P. Kohler (*Amer. Chem. J.*, 1895, **17**, 330—347).—This is a continuation of the work of Remsen and Coates (see preceding abstract). Attempts to separate the two

isomeric chlorides by crystallisation proved futile: but when the mixed chlorides are treated with cold water for some hours crystals form, and may be separated. These crystals are then stable, may be recrystallised from ether or chloroform, and melt at 76°. This substance is probably the symmetrical chloride, $SO_2Cl\cdot C_6H_4\cdot COCl$, and is identical with that described by Remsen and Dohme (Abstr., 1889, 992). When heated at 150°, or in the presence of phosphorus pentachloride at 100°, this substance is decomposed, yielding chlorobenzoic chloride. When aniline acts on the mixed chlorides, about three times as much of the infusible anilide is formed as of the fusible. Aniline acting on the solid chloride (m. p. 76°) in the presence of water yields the fusible anilide in almost theoretical proportion, whilst in the absence of water at 100°, only the anil and aniline hydrochloride are formed. When a solution of the anil in aniline is boiled for some hours, the fusible anilide is formed. The fusible anilide dissolves unchanged in alkalis, but if the alkaline solution is boiled for some time, orthosulphobenzoic acid is formed. It is probably the symmetrical compound $NHPh\cdot CO\cdot C_6H_4\cdot SO_2\cdot NHPh$. The infusible anilide is more resistent towards reagents than the fusible anilide is, and even after continued boiling is reprecipitated from its alkaline solutions unchanged on the addition of an acid. When boiled with benzoic chloride, it yields benzanilide. *Aniline orthosulphanilidobenzoate*, $NHPh\cdot SO_2\cdot C_6H_4\cdot CO\cdot O\cdot NH_3Ph$, crystallising in colourless prisms, is also formed in small quantities during the action of aniline on the chlorides. L. T. T.

Separation of the two Chlorides of Orthosulphobenzoic acid. By Ira Remsen and A. P. Saunders (*Amer. Chem. J.*, 1895, **17**, 347—368; see also three preceding abstracts).—The authors have succeeded in separating these chlorides as follows. The mixed chlorides are treated with light petroleum, and the solution at about 30° is poured off from excess of the chlorides. On cooling this solution to a low temperature, the two chlorides crystallise out, the higher melting chloride (m. p. 76—77°) in square hollow crystals, the lower melting chloride (m. p. 21·5—22·5°) in radiating clusters of delicate, glistening, white needles. The chloride of low melting point even then generally contains some of the isomeride. The crystallisation is best effected by spontaneous evaporation of the petroleum solution in the open air at 0°, or in a current of air at the same temperature. When a chloroform solution of the mixed chlorides is shaken with concentrated aqueous ammonia, the chloride of m. p. 21·5° is completely converted into a substance soluble in water, but the chloride of m. p. 76° is but little attacked. In this way the high melting chloride can be readily obtained pure.

Water acts very slowly on both chlorides, but the same acid is produced in each case. With aqueous ammonia, the liquid chloride yields a sweet substance of the probable formula $CN\cdot C_6H_4\cdot SO_3\cdot NH_4$. This substance crystallises in minute needles melting at 116—120°, and having a bitter taste. With dry ammonia, this substance is also produced together with "saccharin." No similar compounds could be obtained from the high melting chloride. With phenol, both chlo-

rides yield *diphenylic orthosulphobenzoate*, which crystallises in needles melting at 117·5—118·5°, but has a tendency to pass into a coloured substance like phenolphthaleïn. It is, however, doubtful whether its formation from the low boiling chloride is not due to the presence therein of the high melting chloride. By the action of benzene and aluminium chlorides, both chlorides yield first the compound $COPh{\cdot}C_6H_4{\cdot}SO_2Cl$, and finally, with excess, $COPh{\cdot}C_6H_4{\cdot}SO_2Ph$. The former compound yields with potash, *potassium orthobenzoylbenzenesulphonate*, melting at 122—124° when heated quickly, at about 175° when heated slowly. The *ethylic salt* is crystalline, but very unstable. The *acid* crystallises in needles melting at 143—145°. Ammonia forms a *lactime*.

The results leave little doubt that the chloride of m. p. 76—77° has the symmetrical formula, and therefore the chloride of m. p. 21·5—22·5° is probably the unsymmetrical compound. L. T. T.

Action of Nitrous acid on Indene and Coumarone. By Maximilian Dennstedt and Cæsar Ahrens (*Ber.*, 1895, **28**, 1331—1335).—When nitrous acid is led into a cooled ethereal solution of indene, the latter reacts like cinnamene (this vol., i, 456), and yields an α-nitrosite, which melts at 107—109°, and is converted by boiling with absolute alcohol into the β-nitrosite, melting at 136—137°; yellow needles are also obtained of a compound, $C_9H_7NO_2$, very much resembling phenylnitroethylene in appearance; it melts at 141°. Coumarone behaves in a similar fashion, and yields yellow crystals, melting at 126°, of a compound that also resembles phenylnitroethylene; yellow needles, melting at 146—147°, are also obtained, together with the α-nitrosite, which melts at 114—116°. On account of this similarity of behaviour, indene and coumarone must have a similar constitution; it is not impossible that they may be $C_6H_4<\begin{matrix}C{:}CH_2\\ |\\ CH_2\end{matrix}$ and $C_6H_4<\begin{matrix}C{:}CH_2\\ |\\ O\end{matrix}$ respectively. C. F. B.

A New Synthesis of 2′ : 3′-Dimethylindole. By Karl Brunner (*Monatsh.*, 1895, **16**, 183—189).—The substance previously obtained (*Monatsh.*, 1894, **15**, 747) by the action of zinc chloride on the phenylhydrazone of isobutyrylformic acid, and described as scatole, is now shown to be 2′ : 3′-dimethylindole. The same indole derivative has been prepared from *isobutylidenephenylhydrazine*. This is a yellow oily substance which does not solidify at 0°. It distils at 178—180° under a pressure of 68 mm., and rapidly oxidises when exposed to the air. Small quantities of 2′ : 3′-dimethylindole are obtained when the hydrazone is treated with a mixture of sulphuric acid and alcohol. The yield, however, is much better when the hydrazone is heated with twice its weight of powdered zinc chloride at 140—150°. After recrystallisation from light petroleum, the dimethylindole melted at 99°, and was further identified by means of its nitroso-compound and picrate. J. J. S.

Benzophenoneoxime. By Arnold F. Holleman (*Rec. Trav. Chim.*, 1894, **13**, 429—432).—Benzophenoneoxime oxidises spon-

taneously in air to a brown, oily liquid, from which nitric acid and a labile modification of benzophenone can be separated, the latter either by distillation under low pressure with steam or by merely washing with dilute alkali. The action does not take place in an atmosphere of carbonic anhydride, and only very slowly in presence of pure oxygen; in the presence of a small quantity of nitric acid, however, the oxygen is absorbed much more rapidly. The same oxidation is brought about by alkaline permanganate, but with alkaline ferricyanide a colourless oil is obtained, which, except in the presence of nitrous acid, is oxidised by a further quantity of the reagent to a blue liquid soluble in ether.

Labile benzophenone is a colourless oil, boiling at 216—220° (25 mm.), and is converted into the ordinary modification, with development of heat, by the addition of a crystal of the latter. Jn. W.

Formation of Acridine from Orthonitrodiphenylmethane. By Otto Fischer (*Ber.*, 1895, **28**, 1335—1337; compare this vol., i, 52).—The view previously entertained, that the formation of acridine and hydracridine by the action of orthonitrobenzylic chloride on benzene in the presence of aluminium chloride is due to the oxidation of amidophenylmethane formed by the reducing action of the aluminium chloride, is confirmed by the fact that acridine and hydracridine are also formed by the reduction of nitrodiphenylmethane by the usual methods. In these cases, the oxidation is effected by a portion of the unaltered nitro-compound. A. H.

Hexamethyltriamidotriphenylmethane. By Auguste Rosenstiehl (*Compt. rend.*, 1895, **120**, 740—743).—The iodoamido-derivatives of hexamethyltriamidotriphenylmethane previously described (this vol., i, 377), can be accurately estimated by means of standard acid solutions. Sodium hydroxide produces partial substitution of hydroxyl for iodine, but the change is limited by an inverse reaction, and the liquid contains a mixture of methiodide and the amido-base. Silver oxide, on the other hand, acts completely, with formation of the compound $OH{\cdot}C(C_6H_4{\cdot}NMe_3I)_3 + 3H_2O$, which can be accurately titrated with an acid. The alkalinity of these bases is comparable with that of tetrethylammonium hydroxide. The three bases (1) $OH{\cdot}C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NMe_3{\cdot}OH$, (2) $OH{\cdot}C(C_6H_4{\cdot}NMe_3{\cdot}OH)_3$, and (3) $CH(C_6H_4{\cdot}NMe_3{\cdot}OH)_3$ have practically the same properties, so far as their basicity is concerned, and they all decolorise magentas.

There are, however, considerable differences between the basic functions as measured by their behaviour with acids, and whether the phenylic carbinol has been converted into an amido- or an ammonium-derivative, the alcoholic function is modified. In the amido-compound, $OH{\cdot}C(C_6H_4{\cdot}NH_2)_3$, the alcoholic function is the first to react; in the ammonium compounds the ammoniacal function acts first, whilst the alcoholic function no longer reacts with acids, but only with alcohols, to form ethereal salts; and in the amido-ammonium compounds the ammoniacal function acts first, and the alcoholic and amido-functions act almost simultaneously, but when equilibrium

is established the alcoholic function is found to preponderate over that of the amine. C. H. B.

The Fluorindines. By RUDOLF NIETZKI (*Ber.*, 1895, **28**, 1357—1360).—Tetramidobenzene condenses with benzile to form a diorthodiazine of the formula $\begin{matrix}CPh{:}N\\|\\CPh{:}N\end{matrix}>C_6H_2<\begin{matrix}N{:}CPh\\|\\N{:}CPh\end{matrix}$ (Abstr., 1889, 604). This substance, on reduction with zinc dust and acetic acid, yields a blue colouring matter, the *hydrochloride* of which can be obtained in the crystalline form. This is not fluorescent, and is converted by oxidation into the original azine from which it was prepared. It is, therefore, not a fluorindine, although it is the first reduction product of the azine, and must have the formula which Fischer and Hepp (Abstr., this vol., i, 220) ascribe to the fluorindines.

The author further replies to the critical remarks of Fischer and Hepp on several points connected with the constitution and properties of the fluorindines. A. H.

Orthobromphenylnaphthyl Ketone. By R. J. KNOLL and PAUL COHN (*Monatsh.*, 1895, **16**, 207—210).—The ketone,

$$C_6H_4Br{\cdot}CO{\cdot}C_{10}H_7,$$

was obtained by the action of fresh aluminium chloride on a solution of orthobrombenzoic chloride and naphthalene in carbon bisulphide. It was purified by digesting with warm alcohol, and allowing the solution to remain. It forms colourless, monoclinic prisms, sparingly soluble in alcohol and light petroleum, and melts at 89°.

The *sulphonic acid*, which was obtained on warming the ketone with concentrated sulphuric acid, forms colourless needles, which melt at 143°, and dissolve readily in hot water. The *oxime* melts at 154—156°. J. J. S.

Naphthazarin. By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1455—1458).—The author maintains that his previously published experiments fully proved the constitution of naphthazarin, which has only been confirmed by the researches of Zincke and Schmidt (*Annalen*, **286**, 27). The most elegant proof of the constitution of this substance is its preparation from 1 : 2 : 1′ : 4-tetranitronaphthalene by Will. *Tetrahydroxydihydronaphthalene*, $C_{10}H_6(OH)_4$, is obtained by reducing napthazarin with tin and acetic and hydrochloric acids. It crystallises in needles melting at 200°. A. H.

Pinene. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 1344—1353).—The authors have studied the oxidation products of pinene, the crude oil obtained from French oil of turpentine having been used, and only the chief products of the various reactions examined. When oxidised with neutral potassium permanganate solution, pinene, $C\begin{matrix}CHMe\cdot CMe_2\\|\\CH_2\\|\\CH\end{matrix}\begin{matrix}\\\\\\\\\end{matrix}\begin{matrix}\\\\CH\\|\\CH_2\end{matrix}$, is converted

into *pinonic acid*, $CHMe<\begin{matrix}CMe_2\cdot CH\cdot CH_2\cdot COOH\\ CO—CH_2\end{matrix}$, which is a colourless oil, boiling and slightly decomposing at 310—315°. The acid is of a ketonic nature, and yields a mixture of two isomeric *oximes*, $C_{10}H_{16}O_2{:}N\cdot OH$, when treated with hydroxylamine. One of these melts at 125° with loss of water, the other at 160° without loss of water. Pinonic acid is not decomposed by alkaline hypobromite with formation of bromoform and a dicarboxylic acid. When it is treated with nitric acid of sp. gr. 1·18, it yields terebic acid, melting at 174°, and oxalic acid. When oxidised with chromic acid, on the other hand, pinonic acid yields, in addition to terebic acid, isocamphoronic acid, $COOH\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2$, and the dibasic ketonic acid, melting at 128—129°, which has been described by Thiel (Abstr., 1893, i, 423) as isohydroxycamphylic acid, but which the authors name *isoketocamphoric acid*, $COMe\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2$. This acid yields an oxime, and is decomposed by alkaline hypobromite into carbon tetrabromide and isocamphoronic acid.

When pinonic acid is further treated with alkaline potassium permanganate solution on the water bath, it yields a number of interesting oxidation products, some of which are identical with substances which have been observed among the oxidation products of camphor. From the solution of the product in chloroform, crystals are deposited which consist of *dimethyltricarballylic acid*,

$$COOH\cdot CMe_2\cdot CH(COOH)\cdot CH_2\cdot COOH,$$

which melts at 147°, and when heated above its melting point loses water and yields *anhydrodimethyltricarballylic acid*, which forms white crystals melting at 142·5°. The filtrate from the dimethylcarballylic acid contains hydroxytrimethylsuccinic acid, which melts at 141°, and is converted into trimethylsuccinic acid, melting at 145°, by hydriodic acid. The hydroxytrimethylsuccinic acid is accompanied by a lactonic acid, which melts at 143·5°, and is termed by the authors *isocamphoranic acid*, $C_9H_{12}O_6$. When it is warmed with alkalis, it yields the salts of the tribasic *hydroxyisocamphoronic acid*,

$$COOH\cdot CMe_2\cdot CH(CH_2\cdot COOH)\cdot CH(OH)\cdot COOH,$$

which has been prepared in the impure state by Kachler (*Annalen*, **191**, 152) from camphor. Isocamphoranic acid seems to be isomeric with the isocamphorenic acid melting at 226°, obtained by Kachler from isocamphoronic acid by heating with bromine. All these reactions are well expressed by the formulæ given above, which are consistent with the formula recently proposed for camphor by Tiemann (this vol., i, 428). A. H.

Limonene Nitrosochlorides. By Otto Wallach (*Ber.*, 1895, **28**, 1308—1315).—The molecular weight of α- and β-limonene nitrosochlorides have been redetermined in consequence of Baeyer's results (this vol., i, 380). In phenol solution, at the melting point, both are mono-molecular; in benzene solution, at the melting point, the β-compound is bi-molecular, the α-compound partly bi- and partly mono-molecular; the latter is not entirely mono-molecular, even at

the boiling point of the solution. Limonene nitrolanilides, both α- and β-, are mono-molecular in benzene solution, both at the freezing point and at the boiling point. C. F. B.

Action of Hydrogen Peroxide on Coniine and β-Pipecoline. By RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 1459—1466).—The preparation of an amido-aldehyde from coniine by the method used for piperidine (Abstr., 1894, i, 143) does not succeed because of the insolubility of the base. When coniine and hydrogen peroxide are brought together, however, in acetone solution, *α-propyl-δ-amidovaleraldehyde*, $NH_2 \cdot CHPr \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHO$, is produced. It is a colourless syrup, which boils at about 103—105° (at 10 mm. pressure), and has a characteristic odour, quite distinct from that of coniine. It has sp. gr. = 0·9414 at 20°, and the specific rotation $[\alpha]_D = +59{\cdot}95°$. The substance shows the usual reducing properties of an aldehyde, and forms a deliquescent *hydrochloride*, $C_8H_{17}NO,HCl$. Coniine preparations which have been preserved for some time often show slight reducing properties, which are probably due to the formation of a small amount of the aldehyde by the action of the oxygen of the air. When the amido-aldehyde is distilled with potash, it loses water and forms a mixture of coniine and coniceïne. Coniceïne is sometimes formed directly by the action of hydrogen peroxide on an acetone solution of coniine, the base thus produced being different from γ-coniceïne. When the hydrochloride of the aldehyde is treated with sodium hydrogen sulphite, coniinesulphonic acid is precipitated as an oil which soon solidifies to white needles melting at 135°.

In the preparation of the aldehyde from coniine, a certain amount of *butyrylbutyric acid*, $C_3H_7 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, and some acetic acid, is also produced. The former of these melts at 34°, boils at 280—285°, and yields a syrupy *oxime*. β-Pipecoline may be converted in a similar way into *β-methyl-δ-amidovaleraldehyde*, which forms a *hydrochloride* melting at 139°, and a *picrate* which melts at 84°.

A. H.

Piperidylacetal. By RICH. STOERMER and O. BURKERT (*Ber.*, 1895, **28**, 1247—1249; compare Abstr., 1894, i, 556).—The base is most readily purified by means of the ferrocyanide, it is easily soluble, and resembles coniine, being precipitated as an oil when its aqueous solution is warmed. The *hydrobromide* and the additive compounds with propylic bromide and allylic iodide are colourless, crystalline, and extremely deliquescent. The methiodide and ethiodide melt at 121° and 105° respectively, not at 119° and 123°, as previously stated. The *picrate* crystallises in small, yellow needles, and melts at 67°. All attempts to prepare piperidyl aldehyde were unsuccessful. By the action of moist silver oxide on the above methiodide, and distillation of the aqueous solution, a colourless liquid *base* is obtained; it boils at 220°, has an extremely unpleasant fishy smell, and yields only oily salts; it probably corresponds in constitution with dimethylpiperidine, and has the formula $CH_2{:}CH \cdot [CH_2]_3 \cdot NMe \cdot CH_2 \cdot CH(OEt)_2$.

J. B. T.

Piperidylacetone. By RICH. STOERMER and O. BURKERT (*Ber.*, 1895, **28**, 1250—1252).—Chloracetone and piperidine readily react at

the ordinary temperature, forming *piperidylacetone*, $C_5NH_{10}\cdot CH_2\cdot COMe$, a colourless liquid with a somewhat pleasing smell. It boils at 195—197° (uncorr.), gradually becomes yellow, and reduces Fehling's solution and silver solution at ordinary temperatures; the base dissolves in water and the solution becomes turbid when warmed. The yield is 85 per cent. of the theoretical. The *hydrochloride*, $C_8H_{15}NO,HCl$, and the *hydrobromide* are very deliquescent. The *platinochloride* crystallises in large, broad, orange-coloured prisms, and melts at 192—193°. The *aurochloride* is deposited in slender, pale yellow plates, melting at 107—108°. The *methiodide* is crystalline, and melts at 126°. The *oxime* crystallises from water in long needles, from light petroleum in small plates, and melts at 104—105°. The *phenylhydrazone* crystallises in pale yellow plates melting at 59—62°, it is stable in air, but decomposes in a desiccator. The preparation of methylacetylpiperidine by the action of moist silver oxide on the methiodide could not be accomplished, part of the quaternary base is oxidised by the silver oxide, and the remainder is decomposed during the distillation. The *ammonium hydroxide* yields a *chloride* from which the *platinochloride*,

$$(C_5NMeH_{10}\cdot CH_2\cdot COMe)_2PtCl_6,$$

and the *aurochloride* are obtained; both crystallise readily, and melt at 218—219° and 85° respectively. J. B. T.

Synthesis of β-Propylpiperidine. By J. Darnell Granger (*Ber.*, 1895, **28**, 1197—1204; compare R. Funk, Abstr., 1894, i, 34).—*Ethylic γ-phenoxydipropylmalonate*, $OPh\cdot C_3H_6\cdot CPr^{\alpha}(COOEt)_2$, is obtained by heating ethylic γ-phenoxypropylmalonate (*loc. cit.*) with propylic iodide and sodium dissolved in propylic alcohol; it is a colourless, viscous liquid, which boils at 282—283° under a pressure of 100 mm. On hydrolysis with alcoholic potash, it yields the *acid* which sinters at 95°, and melts and decomposes at 104—106·5°. The *ammonium* and *silver* salts are amorphous, the *calcium* salt is crystalline.

When γ-phenoxydipropylmalonic acid is heated at 180—200°, carbonic anhydride is evolved, and *α-propyl-δ-phenoxyvaleric acid* is formed; it is insoluble in water, and separates from ordinary solvents in large, transparent crystals melting at 53—54°. The *nitrile* is obtained by distilling the acid with lead thiocyanate; it is a yellow oil which boils at 318—322°. *β-Propyl-ε-phenoxyamylamine* is formed on reducing this nitrile; the *picrate* melts at 112°, and the *platinochloride* crystallises in yellow needles. When the base is heated with fuming hydrochloric acid for 15 hours at 100°, the *hydrochloride* of *β-propyl-ε-chloramylamine* is formed; the *picrate* melts at 151°.

β-Propylpiperidine is obtained from the foregoing base by heating the hydrochloride with aqueous sodium hydroxide; it is a colourless oil, with the odour of coniine. The vapour produces white fumes when brought into contact with hydrogen chloride; the *picrate* melts at 121·5°, and the *platinochloride* melts at 94° when slowly heated, and at 134° when the temperature rises rapidly. M. O. F.

ν-Methyltetrahydroquinoline (Kairoline) and Tetrahydroquinoline Methohydroxide. By Albert Ladenburg (*Ber.*, 1895,

28, 1171—1173).—The author establishes the identity of kairoline with the base obtained by Ostermayer on treating tetrahydroquinoline methochloride with alkalis. M. O. F.

2′-Phenylquinoline. By Amé Pictet and H. Barbier (*Bull. Soc. Chim.*, 1895, [3], **13**, 26—28).—When acetophenone and formanilide are boiled together for 30 hours, the product is not 4′-phenylquinoline, as might be expected, but the 2′-compound. This is conveniently isolated by means of the *mercurochloride*, a crystalline substance melting at 231°. The free base melts at 85°, and shows all the properties of 2′-phenylquinoline. The mechanism of formation thus resembles that of acridine from formyldiphenylamine, and would seem to point to the existence of a para-bond between nitrogen and carbon in the pyridine nucleus. Jn. W.

Benzylquinoline. By Leopold Rugheimer and W. Kronthal (*Ber.*, 1895, **28**, 1321).—*Benzylquinoline*, $C_9NH_6{\cdot}CH_2Ph$, was prepared by heating benzoyltetrahydroquinoline with benzaldehyde. It crystallises in large tablets, and yields a *hydrochloride*, yellow *platinochloride*, silky *sulphate*, and yellow *picrate*; the last melts at 161·5°. C. F. B.

Ethylglyoxalidine and Propylglyoxalidine. By E. Klingenstein (*Ber.*, 1895, **25**, 1173—1176; compare this vol., i, 73).—*Ethylglyoxalidine*, $\begin{matrix}CH_2-N\\ |\\ CH_2{\cdot}NH\end{matrix}\!\!>\!CEt$, is obtained by distilling a mixture of ethylenediamine hydrochloride (10 grams) and sodium propionate (18 grams); it boils at 144—148° under a pressure of 95 mm., and solidifies when cooled. The *hydrochloride* and *hydrobromide* are crystalline and hygroscopic; the *aurochloride* melts at 171—172°, and the *platinochloride* crystallises in reddish-yellow prisms, and melts at 198°. The *mercurochloride* has the composition $C_5H_{10}N_2,HCl,5HgCl_2$, and melts at 169—171°. The *picrate* melts at 134—136°, and the *benzoyl* derivative at 242°; the *urate* has not been obtained free from uric acid. *Dipropionylethylenediamine* forms the intermediate product in the preparation of ethylglyoxalidine; it melts at 160—162° and boils at 220—230° under a pressure of 95 mm.

Propylglyoxalidine is obtained from ethylenediamine hydrochloride and sodium butyrate; it is a colourless, hygroscopic liquid which boils at 134—140° under a pressure of 23 mm., and solidifies when cooled. The *hydrochloride* and *hydrobromide* are hygroscopic; the *aurochloride* melts at 126—127°, and the *platinochloride* crystallises in red prisms melting at 162—164°. The *mercurochloride* melts at 163—165°, and the *picrate* crystallises in long needles, and melts at 124—126°; the *urate* has not been obtained free from uric acid. In preparing propylglyoxalidine by the method indicated, *dibutyrylethylenediamine* is also formed. M. O. F.

Dimethylglyoxalidine and Methylethylglyoxalidine. Resolution of Propylenediamine into its Optical Components. By Georg Baumann (*Ber.*, 1895, **28**, 1176—1180).—1 : 4-*Dimethylglyox-*

alidine, $\begin{matrix}CHMe\cdot NH\\ |\\ CH_2\text{——}N\end{matrix}\!\!>\!CMe$, is obtained by distilling a mixture of propylenediamine hydrochloride and sodium acetate (2 mols.), the diacetyl-derivative being produced at the same time. The base is a pale yellow liquid which boils at 125° under a pressure of 22 mm.; it is hygroscopic, and is readily miscible with all ordinary solvents. The *benzoyl* derivative melts at 197°, and the *aurochloride* crystallises in yellow leaflets melting at 175°; the *picrate* melts at 140°, and the *mercurochloride*, which has the composition $C_5H_{10}N_2,HCl,6HgCl_2$, melts at 176°.

4 : 1-*Methylethylglyoxalidine* is obtained from propylenediamine hydrochloride and sodium propionate; it boils at 130° under a pressure of 62 mm., and is readily soluble in water. The *dipropionyl*-derivative is formed at the same time; it crystallises in small, white needles and melts at 165°. The *hydrochloride*, *hydrobromide*, and *tartrate* are hygroscopic syrups, and the *benzoyl*-derivative melts at 205°. The *aurochloride* and *platinochloride* melt at 125° and 188° respectively; the *picrate* melts at 132°, and the *mercurochloride*, which has the composition $C_6H_{12}N_2,HCl,5HgCl_2$, melts at 172°.

4-*Methylglyoxalidine* is obtained from propylenediamine hydrochloride and sodium formate; the *aurochloride* melts at 166—168°, and the other salts are extremely soluble in water.

Lævorotatory propylenediamine is obtained from the tartrate which melts at 141°; the specific rotatory power is −19·11° at 24·3°. The *picrate* forms yellow crystals and melts at 237°. M. O. F.

Antipyrine Derivatives. By Adolf Schuftan (*Ber.*, 1895, **28**, 1180—1187).—*Methylenediantipyrine*,

$$\begin{matrix}NPh\text{—}CO\\ |\\ NMe\cdot CMe\end{matrix}\!\!>\!C\cdot CH_2\cdot C\!<\!\begin{matrix}CO\text{—}NPh\\ |\\ CMe\cdot NMe\end{matrix}$$

is obtained by heating a mixture of antipyrine and formaldehyde at 120°; it is also formed when benzylidenediantipyrine (*loc. cit.*) is heated in sealed tubes with formaldehyde and zinc chloride for six hours at 120°. It crystallises in white, lustrous leaflets, and melts at 177°. The *hydrochloride* and *sulphate* crystallise in colourless needles; the *platinochloride* forms long, reddish-yellow needles, and becomes black at 200°, without undergoing fusion. The *aurochloride* crystallises in reddish-brown plates, melting and decomposing at 179°; the *picrate* melts at 185°, and the *tetrabromide* forms pale yellow needles, which melt and decompose at 140°.

Ethylidenediantipyrine crystallises in white nodules, and in the anhydrous state melts at 153°; a specimen dried in the exsiccator melted at 110°, losing $1H_2O$. The *hydrochloride* crystallises in slender, white needles, and melts at 134°, the sulphate is sparingly soluble in cold water, and separates from dilute sulphuric acid in slender needles. The *platinochloride* does not melt at 200°, at which temperature, however, it turns black; the *picrate* crystallises in yellow needles.

Hydroxybenzylidenediantipyrine is obtained on heating a mixture

of antipyrine and salicylaldehyde for eight hours at 120°. The base separates from methylic alcohol in colourless, transparent prisms, and contains $1H_2O$, which is not lost at 110°; it melts at 180—190°. The *hydrochloride* crystallises in colourless needles, and the *picrate* in yellow needles which melt and decompose at 216°; the *platinochloride* forms reddish-yellow needles. M. O. F.

Cinchonine and Cinchotenine. By ZDENKO H. SKRAUP (*Monatsh.*, 1895, **16**, 159—179; compare Abstr., 1880, 409).—Cinchotenine is obtained by oxidising cinchonine with potassium permanganate.

$$C_{19}H_{22}N_2O + O_3 = C_{18}H_{20}N_2O_3 + CH_2O_2.$$

Formic acid is the other product of oxidation, and this shows that one of the carbon atoms of cinchonine must be in a more exposed position than the others. According to Schützenberger, cinchonine contains a hydroxyl group, as it yields a benzoyl derivative. The author shows that this hydroxyl is also contained in cinchotenine, since benzoylcinchonine when oxidised gives benzoylcinchotenine. Cinchotenine further contains a carboxyl group, and reacts as a saturated compound; cinchonine, on the other hand, reacts as an unsaturated compound, and contains no carboxyl group. The two are best represented as follows.

$OH\cdot C_{17}H_{18}N_2\cdot CH{:}CH_2$	$OH\cdot C_{17}H_{18}N_2\cdot COOH$
Cinchonine.	Cinchotenine.

Benzoylcinchonine melts at 75°, and is very soluble in ether and benzene. It is slowly hydrolysed by boiling acids, much more readily by alkalis. The *hydrochloride*, $C_{19}H_{21}N_2OBz,HCl$, crystallises in long needles, which melt at 206—207°. The dihydrochloride, $C_{19}H_{21}N_2OBz,2HCl$, loses hydrogen chloride at 120°. The disulphate is amorphous, and is not decomposed by heating to 140°, whereas cinchonine disulphate itself is readily decomposed at this temperature, and yields cinchonicine.

Benzoylcinchotenine, $C_{18}H_{19}N_2OBz$, does not readily crystallise if it contains traces of impurities. When quite pure, it forms short, colourless prisms, which melt at 175—178°. It forms a crystalline hydrochloride, and when hydrolysed gives benzoic acid and cinchotenine.

The *ethylic* salt of *cinchotenine* is readily obtained as a hydrochloride by saturating an alcoholic solution of cinchotenine with dry hydrogen chloride. This *hydrochloride* melts at 235°, and the ethylic salt itself at 210°. This ethereal salt reacts vigorously with benzoic chloride to form a *benzoyl* derivative, $C_{15}H_{16}N_2O_3EtBz,2HCl$. The corresponding *acetyl* derivative has also been prepared. This indicates that there are two replaceable hydrogen atoms in cinchotenine, one probably in a hydroxyl group, and the other in a carboxyl group.

Commercial cinchonine, when oxidised with chromic acid mixture, gave about 3 per cent. of cincholeuponic acid, $C_6H_{13}NO_4$. As it was doubtful whether this acid was derived from the cinchonine itself, or

from the impurities, the author has oxidised pure cinchotenine sulphate with chromic acid, and finds that the cincholeuponic acid is one of the products. It thus follows that the acid is a derivative of cinchonine. When the hydrochloride of the acid is suspended in alcohol and the mixture saturated with dry hydrogen chloride, *ethylic cincholeuponate*, $C_8H_{11}NO_4Et_2,HCl$, is formed, which melts at 164—165°. This indicates that the acid contains two carboxylic groups. The investigation of this acid, and also of merochinene and other allied substances, is being continued. J. J. S.

Synthesised Colloïds and Coagulation. By JOHN W. PICKERING (*J. Physiol.*, 1895, **18**, 54—66).—Certain colloïd substances, first prepared by Grimaux, exhibit reactions which are very similar to those of proteïds, especially of the globulin class. Two, named *A* and *B*, are prepared by the action of phosphorus pentachloride on metamidobenzoic acid at different temperatures; the colloïd *C*, by the action of a current of ammonia at 170° on aspartic anhydride. Each, when dried, resembles dried serum albumin; they dissolve in water, forming pale straw-coloured, opalescent solutions. Each gives the xanthoproteïc reaction, and *C* gives a well-marked violet coloration with copper sulphate and potash. In the presence of minute quantities of salts (such as soluble salts of barium, strontium or calcium, sodium chloride, magnesium sulphate, or ammonium chloride), their solutions coagulate on heating to 75°. This is retarded by potassium acetate, sodium sulphate, or excess of glycerol. The passage of a current of carbonic or sulphuric anhydride restores the coagulability destroyed by glycerol. The colloïds are removed from solutions by saturation with magnesium sulphate, ammonium sulphate, or sodium chloride. The separated solid rises to the surface, and readily redissolves on the addition of water. Boiling water renders the colloïds insoluble. Treatment of the insoluble product with ammonia and evaporation in a vacuum regenerates the colloïd, forming a soluble substance which yields all the reactions (including the physiological action immediately to be mentioned) of the original substance.

In the presence of salts, carbonic anhydride precipitates the colloïds, and these redissolve like globulins on substituting a current of air for the carbonic anhydride.

Colloïd *C* is digested by pepsin readily, the solution giving the colour reactions of peptone. Colloïd *A* is slightly digestible, *B* is indigestible.

Each when injected intravenously into rabbits causes death by intravascular clotting, 5 to 20 c.c. of a 1·5 per cent. solution being usually fatal. They do not induce coagulation in extravascular (salted) plasma. Full details of these experiments is deferred.

W. D. H.

Organic Chemistry.

Preparation of Ethylic Bromide. By ADRIAN (*Chem. Centr.*, 1895, i, 20; from *Mon. Sci.*, 1894, [4], **8**, 834).—The French *Codex medicamentarius* directs the preparation of pure ethylic bromide by re-distilling the product obtained by heating a mixture of alcohol, sulphuric acid, and potassium bromide. Following the prescribed directions, however, a product is obtained which contains up to 15 per cent. of ether; the author removes the latter by shaking with a small quantity of sulphuric acid which dissolves the ether, and may be separated. On shaking with dilute alkali and distilling with 10 per cent. of sweet almond oil, pure ethylic bromide is obtained.

W. J. P.

Analogy between the Behaviour of Halogen Alkylenes towards Sodium and like Metals, on the one hand, and towards Mercaptides on the other hand. By ROBERT OTTO and K. MÜHLE (*J. pr. Chem.*, 1895, [2], **51**, 517—521; compare this vol., i, 286).—A table is given illustrating the analogy indicated by the title. From this it is seen that all halogen alkylenes which contain fewer than four carbon atoms, yield the corresponding alkylene, both when they react with sodium or similarly active metals, and when they react with sodium mercaptide; but not all of those which contain a greater number of carbon atoms than four behave in this way with sodium, although they may so behave with sodium mercaptide.

A. G. B.

Copper and Manganese Cyanides. By PAUL STRAUS (*Zeit. anorg. Chem.*, 1895, **9**, 6—18).—Potassium manganocyanide is best prepared by Christensen's method (*J. pr. Chem.*, **31**, 171), but using the following proportions: 15 grams of manganese acetate dissolved in 90 grams of cold water is added to a solution of 25 grams of potassium cyanide in 50 grams of water. A green precipitate is obtained which is redissolved by heating on the water bath with the addition of 25 grams of potassium cyanide. On cooling, the potassium manganocyanide crystallises in beautiful, dark violet, quadratic tablets. It effloresces on exposure to the air, undergoing partial oxidation, is insoluble in water, and, when treated with water, decomposes into potassium cyanide and $KMn(CN)_3$.

Potassium manganicyanide is also prepared, according to Christensen's method, by adding normal manganese phosphate (15 grams) to a solution of potassium cyanide (40 grams) in 150 grams of water. A dark brown precipitate is obtained, which is redissolved by the addition of 20 grams of potassium cyanide. It crystallises in reddish-brown needles, and is stable on exposure to air.

Potassium manganocyanide, when quite free from potassium cyanide, is insoluble in water, but is at once decomposed by it, and the author was unable to obtain ferrimanganocyanide by treating it with ferric chloride. In presence of small quantities of potassium cyanide, the

manganocyanide is soluble, but the blue precipitate obtained with ferric chloride is not pure ferrimanganocyanide.

Ferromanganicyanide, $Fe_3Mn_2(CN)_{12}$, is obtained by adding a solution of ferrous sulphate to a solution of potassium manganicyanide at a temperature not exceeding 5°, and in an atmosphere of hydrogen. It is a dark blue precipitate, which becomes of a dirty colour on exposure to air, and decomposes with evolution of cyanogen. When heated with soda, it is converted into sodium ferrocyanide with precipitation of manganese and iron. When allowed to remain over sulphuric acid in an atmosphere of hydrogen, it changes to a greenish-black powder, and loses cyanogen.

Potassium cupromanganocyanide, $K_2Cu_2Mn(CN)_6$, is obtained by adding an aqueous solution of manganese acetate to a solution of potassium copper cyanide, $(KCN)_6(CuCN)_2$. It crystallises in white cubes, is stable when damp, but oxidises and turns brown when dried over sulphuric acid. It is insoluble in water, is completely decomposed by boiling with dilute acids, and partially so by alkali carbonates and hydroxides.

Sodium cupromanganocyanide, obtained in a similar way to the potassium salt, crystallises in four-sided prisms, and is much more stable and soluble in water than the potassium salt.

Ammonium cupromanganocyanide is obtained by treating the sodium salt with ammonium nitrate. It crystallises in six-sided prisms, and is stable on exposure to air.

Potassium cuprocupricyanide, $K_2Cu_3(CN)_6$, is obtained by adding a concentrated solution of copper sulphate to a solution of potassium copper cyanide, $(KCN)_6(CuCN)_2$, and heating the mixture for a short time on the water bath. It crystallises in six-sided domes.

The author has attempted to prepare compounds similar to the above from nickel and cobalt salts. When potassium copper cyanide is treated with nickel nitrate a *double salt*, of the composition $Cu_2(CN)_2,2KCN,2[Ni(CN)_2,2KCN]$, is obtained. It crystallises in six-sided tablets, and, when treated with water, is decomposed into its constituent salts, the potassium nickel cyanide passing into solution. The corresponding *cobalt salt* is obtained in a similar way, and, when heated with excess of potassium copper cyanide, is converted into potassium cobalticyanide. E. C. R.

Ferrocyanides. By J. Messner (*Zeit. anorg. Chem.*, 1895, **9**, 126—143).—The constitution of Prussian blue and Turnbull's blue cannot with certainty be determined either by analysis or by an examination of their decomposition products. Turnbull's blue, which according to the method of its formation is ferrous ferricyanide, is not decomposed by alkalis into ferrous hydroxide and potassium ferricyanide, but into ferric hydroxide and potassium ferrocyanide; that is, it yields the same decomposition products as Prussian blue. The decomposition of the blue with borax, sodium phosphate and the oxides of light and heavy metals, gave no definite results. When treated with cold concentrated hydrochloric acid, the blues are partially dissolved, and the yellow solution, when mixed with water, yields a precipitate of the blue, but decomposition also takes place,

and iron always remains in the solution. Prussian blue treated in this way gave a solution containing ferric oxide together with small quantities of ferrous oxide; Turnbull's blue gave a solution containing ferrous oxide and a small quantity of ferric oxide. The quantitative analysis of the two blues gives no definite result, partly because the theoretical percentage composition [for Prussian blue, $Fe_4(FeC_6N_6)_3$; for Turnbull's blue, $Fe_3(FeC_6N_6)_2$] of both is very similar, and partly because the compounds are very difficult to obtain pure. The author gives the results of a number of analyses made with different preparations.

The constitution of Prussian green, for which numerous formulæ have been proposed, is also not determined by its decomposition products. When decomposed by alkalis, it yields ferric hydroxide and potassium ferrocyanide and ferricyanide. Ferricyanides, however, are partially converted by alkalis into ferrocyanides. The analyses of various preparations of Prussian green indicate that it is a ferric ferricyanide, $Fe(FeC_6N_6)$. The purest preparation is obtained by saturating a solution of potassium ferricyanide with chlorine, taking care to exclude light, then heating the solution to boiling, allowing it to cool in a current of chlorine, and finally washing out the chlorine with cold water.

Williamson's violet is prepared by careful oxidation of ferropotassium ferrocyanide, $K_2Fe(FeC_6N_6)$. The best method, according to the author, is to use a ferric salt as the oxidising agent. The analyses of various preparations gave widely different results, and the author was unable to determine the composition with certainty. The composition, $KFe(FeC_6N_6)$, is based on the formation of the compound by the oxidation of ferropotassium ferrocyanide.

Besides the copper ferrocyanides already described (this vol., i, 405), the author has prepared the following. *Lithium cuproferrocyanide*, obtained by boiling cuprous cyanide with lithium ferrocyanide and lithium sulphite in an atmosphere of hydrogen, crystallises in colourless six-sided prisms. *Lithium cupriferrocyanide*, obtained by boiling copper ferrocyanide free from alkali with lithium ferrocyanide, crystallises in small, quadratic red plates or brownish-red needles. *Potassium cupriferrocyanide* is obtained by boiling cuprous cyanide with excess of potassium ferricyanide according to the equation $CuCN + 2K_3(FeC_6N_6) = K_2Cu(FeC_6N_6) + K_4(FeC_6N_6) + CN$. It crystallises in brownish-red, quadratic prisms. E. C. R.

Occurrence of Titanium Cyanonitride in Ferromanganese. By T. W. Hogg (*Chem. Centr.*, 1895, i, 149; from *Engin. Min. Jour.*, 1893, 664).—Titanium cyanonitride, and sometimes also titanium nitride and carbide, are contained in most samples of ferromanganese. The cyanonitride is obtained by dissolving the ferromanganese in dilute nitric acid, powdering the carbonaceous residue, and washing until only the copper coloured cyanonitride remains; more than 0·032 per cent. of this substance can never be separated from the alloy. Titanium cyanonitride thus prepared consists of microscopic, brilliant crystals of density 4·1—5·1, and contains 60—80 per cent. of titanium. W. J. P.

Carbon Tetrachloride and the Purification of Methylated Alcohol. By MAXIME CARI-MANTRAND (*Compt. rend.*, 1895, **120**, 1063—1064).—The alcohol is mixed with one-fourth its volume of carbon tetrachloride, and afterwards with a sufficient quantity of a saturated solution of sodium chloride (about $2\frac{1}{2}$ times the original volume) to precipitate the carbon tetrachloride. After repeated vigorous agitation the carbon tetrachloride is separated and retains all the impurities except methylic alcohol and acetone. The saline solution is mixed with sufficient water to reduce the alcoholic strength to 25°, and is then fractionated with a sufficient condensing column to give alcohol of 96·5° to 97° at one distillation. All the product that distils above 78° is pure alcohol.

The carbon tetrachloride can be purified by agitating with sulphuric acid at 66° and afterwards washing with water. The salt solution after cooling can be used again. C. H. B.

Impurities in Ethylic Ether. By ADRIAN (*Chem. Centr.*, 1895, i, 20; from *Mon. Sci.*, 1894, [4], **8**, 835).—Ethylic ether always contains acetaldehyde as an impurity, which can be at once detected and removed by passing dry ammonia into the dried ether when aldehyde-ammonia crystallises out, being insoluble in dry ether; after filtering this off, the ether is shaken with sulphuric acid, and subsequently distilled from potassium carbonate. W. J. P.

Platinum Compounds of Ethylic Sulphide. By PETER KLASON (*Ber.*, 1895, **28**, 1493—1500).—Blomstrand (Abstr., 1889, 230) has described two isomeric forms of platosethylsulphine chloride, the α-compound, melting at 81°, and the β-compound, melting at 106°. The author finds that, when pure, the two isomerides melt at the same temperature, 108°, and that they readily pass one into the other. The α-chloride only reacts slowly with alcoholic silver nitrate solution, whilst the β-chloride appears to react as rapidly as sodium chloride, and a measurement of the electrical conductivity of solutions of the two in dilute alcohol shows that the β-compound is a much better conductor than the α-chloride. The bromide melts at 124°, and yields the α-chloride when treated in the cold with silver chloride. It may be prepared from either the α- or β-chloride by the action of potassium bromide, and is isomorphous with the α-chloride. The α-chloride is converted by dry ammonia in chloroform solution into a salt of the formula $Pt(NH_3)_3Et_2SCl_2 + H_2O$, which decomposes on heating, leaving a residue containing ammonium platinosochloride and the triammonioplatinous chloride of Clève. The β-chloride behaves in a similar manner, yielding an isomeric substance, $PtEt_2S(NH_3)_3Cl_2 + H_2O$, which also decomposes when heated, but forms an isomeric triammonioplatinous chloride.

When either of the two chlorides is treated in alcoholic solution with ethylic hydrosulphide or phenylic hydrosulphide, the chlorine atoms are replaced by the thio-radicle, and unstable compounds are formed, which cannot be isolated in the pure state, but rapidly lose ethylic sulphide. In chloroform solution, on the other hand, ethylic hydrosulphide forms the compound, *ethylsulphideplatosothioethylic*

chloride, $Et_2S{\cdot}Pt{\cdot}SEtCl$, which separates from chloroform on the addition of alcohol in yellow crystals melting at 124°. Bromine converts it into *ethylsulphidebromoplatosothioethylic chloride*,

$$Et_2SBr_2PtSEtCl,$$

which is an almost insoluble red crystalline powder.

Ethylsulphideplatosothioethylic chloride is converted by ammonia in chloroform solution into *ammonioplatosothioethylamine chloride*, $EtS{\cdot}Pt(NH_3){\cdot}NH_3Cl$, which crystallises in stellate groups of needles, and gives a crystalline precipitate with potassium chloroplatinite of *ammonioplatosothioethylamine chloroplatinite*. A. H.

Glycerols from Secondary Allylic Alcohols. By H. Fournier (*Bull. Soc. Chim.*, 1895, [3], **13**, 121—124).—These can be prepared by Wagner's method, namely, oxidation with 1 per cent. permanganate, and are yellowish, viscid liquids, soluble in water, alcohol, and ether. The triacetates are colourless, and much more mobile.

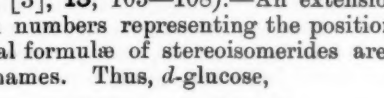
1 : 2 : 4-*Trihydroxyhexane*, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CHEt{\cdot}OH$, from ethylallylcarbinol, boils at 190—192° (30 mm.); the *triacetate* boils at 168—169° (20 mm.), or at 273—276° (atmos.); and has a sp. gr. = 1·086 at 21°.

Trihydroxyisoheptane, $CHMe_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, from isopropylallylcarbinol, boils at 194—197° (30 mm.); the *triacetate* boils at 176—180° (20 mm.), or at 276—280° (atmos.), and has sp. gr. = 1·071 at 24°.

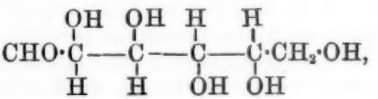
Trihydroxyisoctane, $CHMe_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, from isobutylallylcarbinol, boils at 198—200° (30 mm.); it solidifies in a mixture of solid carbonic anhydride and ether, but melts again at about 0°, and not at 50°, as stated by Wagner (Abstr., 1894, i, 563); the *triacetate* boils at 179—180° (20 mm.), or at 288—290° (atmos.), but in the latter case decomposes slightly; sp. gr. = 1·049 at 24°.

Trihydroxyphenylbutane, $CHPh(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, from phenylallylcarbinol, decomposes when distilled, even under very low pressure; the *triacetate* is a viscid, faintly odorous liquid, boiling at 221—222° (20 mm.). Jn. W.

Nomenclature of Stereoisomerides. By Robert Lespieau (*Bull. Soc. Chim.*, 1895, [3], **13**, 105—108).—An extension of the Geneva system, in which numbers representing the positions of the groups in the conventional formulæ of stereoisomerides are incorporated in their systematic names. Thus, *d*-glucose,



is hexapentol-2456, 3-al, whilst l-mannose,



is hexapentol-236, 45-al, the numbers being read from the left to the right of the chain, and the upper and terminal numbers preceding, and being separated by a comma from the lower. Optical isomerides are characterised by identical groups in inverted order; *d*-mannose, for example, is hexapentol-456,23-al (the 6 of the CH_2·OH-group remaining unchanged). When all the groups are on one side of the chain, the comma is placed at the end of the formula, for example, hexapentol 23456-al, (? at the end of the numbers -23456,-al). In compounds which, like the hexitol derived from *d*-glucose and *d*-gulose, are symmetrical as to the terminal groups, the formula may be arranged and numbered in two distinct ways, namely, in the case cited, as hexanehexol-146,235, or -12456,3. Such hidden identities may be detected by adding one set of numbers (not including the terminal numbers) to the other set inverted, when the sum of every pair will be the same; thus, in the above case, 4235 + 3542 = 7777.

Jn. W.

Note by Abstractor.—Identities concealed by double formulæ would be detected on inspecting the graphic formulæ; a precisely similar difficulty occurs with polysubstituted ring-compounds.

Constitution of Glucosides and Glucoses. By Leo Marchlewski (*Ber.*, 1895, **28**, 1622—1623).—The author defends his view of the constitution of glucose and the glucosides (Abstr., 1894, i, 104) against the criticism of E. Fischer (this vol., i, 438).

C. F. B.

Molecular Modifications of Glucose. By Charles Tanret (*Compt. rend.*, 1895, **120**, 1060—1062).—Dubrunfaut has shown that freshly prepared solutions of glucose have double the rotatory power possessed by solutions that have been prepared for some time, and has isolated the two forms, one having a rotatory power $[\alpha]_D = +106°$, and the other $[\alpha]_D = +52°$. The author distinguishes the former as α-glucose, and the latter as β-glucose, and he has obtained a third modification, γ-glucose, the rotatory power of which is only $[\alpha]_D = +22{\cdot}50°$.

α-Glucose is the form in which glucose always crystallises from cold water, and, under certain conditions, from alcohol; when dissolved in water, it changes into β-glucose in a few minutes if boiled, in seven or eight hours at 15°, and in more than 30 hours at 0°; but the change takes place immediately in the cold if 1 per cent. of potassium hydroxide is added. In alcoholic solutions, the change is less rapid the more concentrated the alcohol, and in absolute alcohol only 90 per cent. is converted even after boiling for several hours.

It is obvious that the so-called solubilities of α-glucose in water or alcohol are really solubilities of β-glucose, or of a mixture of the two.

β-Glucose is obtained by heating a concentrated solution of very pure glucose on a water bath, with constant agitation, or by adding a fragment of a previous crystallisation to α-glucose fused at 100°. If the product obtained from hot liquids is dissolved in its own

weight of cold water, gradually mixed with a large quantity of absolute alcohol cooled at 0°, and vigorously stirred, β-glucose separates before it has had time to change into α-glucose.

β-Glucose dissolves rapidly in half its weight of water at 19°, and after about an hour the liquid begins to deposit α-glucose. The same change takes place in presence of a quantity of water insufficient to dissolve the glucose, and also partially in a non-saturated alcoholic solution. The solubility of β-glucose in alcohol decreases with the concentration of the alcohol.

γ-*Glucose* is formed in small quantity when amorphous glucose is heated at 100°, but the most favourable temperature is 110°, and the best plan is to heat at this temperature for seven or eight hours a highly concentrated solution of glucose spread on plates. The crude product is dissolved in its own weight of cold water, decolorised with animal charcoal, and mixed with sufficient absolute alcohol to bring the alcoholic strength to 90° or 95°, according to the quantity of γ-glucose present, as shown by the polarimeter; if the solution is then vigorously stirred, γ-glucose separates. The treatment is repeated if necessary.

γ-Glucose changes completely into β-glucose under the same conditions as α-glucose, and in about the same time. It dissolves immediately in 0·75 times its own weight of water at 19°. The action of alcohol is similar, and if solutions of any of the three glucoses in alcohol of the same concentration are heated for a sufficient length of time, the same rotatory power is obtained. The solubility of γ-glucose in alcohol of various concentrations is about half that of β-glucose.

Cryometric observations show that all three modifications have the same molecular weight. C. H. B.

Resolution of Starch by the Action of Oxalic Acid. By Carl J. Lintner and Georg Düll (*Ber.*, 1895, **28**, 1522—1531).—In continuation of their investigation of the products of the hydrolysis of starch, the authors have examined the action on it of oxalic acid. Numerous experiments were made with other acids, but this was selected on account of its relatively great activity, the ease with which it can be completely removed, and because, unlike sulphuric acid or hydrochloric acid, it does not cause the formation of reversion products. Saloman's observation that dextrose is readily formed by the action of oxalic acid on starch is confirmed; the best results are obtained as follows. Starch (100 grams) is warmed with water (500 c.c.) containing oxalic acid (2 grams), and the solution heated for an hour under three atmos. pressure. In the following experiments potato starch was always employed.

Amylodextrin appears to be formed, together with compounds of higher molecular weight, almost as soon as the starch has dissolved; the best results were obtained with the following proportions: starch (100 grams), water (400 c.c.), oxalic acid (0·2 gram), heated for ½ hour under 2½ atmos. pressure. The compound readily forms spheroïdal crystals, consisting of aggregates of needles, but this is no test of purity, as much mother liquor is present; in general pro-

perties, the compound resembles that obtained by the action of diastase (Abstr., 1894, i, 5).

Erythrodextrins.—These were obtained by heating the starch (100 grams) with water at 65° (400 c.c.), and 5 per cent. oxalic acid solution (8 c.c.) for one hour under 1·5 atmos. pressure; the product, after treatment with calcium carbonate, gave a reddish-brown iodine reaction; it was evaporated and fractionally precipitated with alcohol; eventually the following products were obtained. *Erythrodextrin* I $(C_{12}H_{20}O_{10})_{18},H_2O$, $[\alpha]_D = 196°$, R = about 3 per cent. (M); iodine reaction, with dilute solution, reddish-violet; forms spheroïdal crystals, is sparingly soluble in alcohol (60 per cent.), and probably identical with the compound formed by the action of diastase. *Erythrodextrin* IIα $(C_{12}H_{20}O_{10})_9,H_2O$, $[\alpha]_D = 194°$, R = about 8 per cent. (M); with dilute iodine solution becomes reddish-brown; with concentrated solution (twice normal) in presence of sulphuric acid a pure blue precipitate is formed (the presence of amylodextrin causes a blue colour with dilute solutions); this, after filtration and washing with dilute sulphuric acid, dissolves in water, and the colour slowly changes to reddish-brown; the change is accelerated by dilution, and the addition of much water causes the colour to disappear completely. The compound is sparingly soluble in cold water, and very readily forms spheroïdal crystals. *Erythrodextrin* IIβ, isomeric with the preceding compound, gives a pure reddish-brown coloration with iodine solution, dilute or concentrated, with or without the addition of sulphuric acid; it is insoluble in alcohol (75 per cent.), and was not observed to form spheroïdal crystals. The erythrodextrins IIα and IIβ, although not previously observed by the authors, are probably identical with those recently prepared by Nittelmeier.

Achroodextrins.—Starch (120 grams), water at 65° (400 c.c.), and 5 per cent. oxalic acid solution (20 c.c.) are mixed, and heated for one hour under $1\frac{1}{2}$ atmos. pressure. The osazone test showed that dextrose (21 per cent.), isomaltose (34 per cent.), and dextrin (45 per cent.) were present in the crude product. Maltose could not be detected either in this or in any other experiment. After purification and fractionation of the liquid, two compounds only could be isolated. Achroodextrin I agrees closely in properties with the corresponding compound previously described (*loc. cit.*), the mol. weight = 1800—2000, specific refractive power = 192°. *Achroodextrin* II, $(C_{12}H_{20}O_{10})_3,H_2O$, is crystalline; $[\alpha]_D = 180°$, Rm = 24. It is extremely difficult to purify, and is probably identical with Mittelmeier's "primary achroodextrin."

The following table shows the compounds which have been isolated by the action of oxalic acid and diastase respectively on starch. It is not implied that they are formed in the order mentioned, and the authors consider that the enunciation of any hypotheses relating either to this or to the manner of their formation would be premature until more experimental evidence has been accumulated.

Compounds formed from starch.

With oxalic acid.	With diastase.
Amylodextrin.	Amylodextrin.
Erythrodextrin I.	Erythrodextrin I.
Erythrodextrin II$_\alpha$.	—
Erythrodextrin II$_\beta$.	—
Achroodextrin I.	Achroodextrin I.
Achroodextrin II.	Achroodextrin II.
Isomaltose.	Isomaltose.
—	Maltose.
Dextrose.	—

J. B. T.

New Type of Lignocellulose. By W. C. Hancock and O. W. Dahl (*Ber.*, 1895, **28**, 1558—1563).—The stem of *Aeschynomene Aspera* is composed of a lignocellulose which differs in some respects from all other members of this class which have yet been described. In composition, behaviour to alkaline agents, absorption of chlorine, &c., it appears to act as a typical lignocellulose. It, however, does not give the characteristic yellow coloration with aniline which is usually given by the lignocelluloses, and is therefore free (except in isolated cells which do give the coloration) from the compounds of aldehyde- or quinone-like character which generally accompany lignocellulose. It, moreover, does not give the phloroglucinol reaction for the pentosanes, although it yields furfuraldehyde when treated by the method of Flint and Tollens. The reaction with iodine and hydriodic acid resembles that of cellulose, a deep blue colour being produced. A. H.

Reduction of Hexamethylenetetramine to Trimethylamine. By Marcel Delepine (*Bull. Soc. Chim.*, 1895, [3], **13**, 135—140).—Hexamethyleneamine is reduced by zinc dust and acetic acid, not to ammonia and methylamine, as stated by Trillat and Fayollat (Abstr., 1894, i, 64), but to ammonia and trimethylamine, and the formation of the triamine takes place equally well under the conditions described by those authors as when the pure hexamine is used. The trimethylamine was characterised by means of its bismuthiodide, methiodide, and platinochloride.

These results confirm the author's formula for hexamethylenetetramine (this vol., i, 327), from which, as each of the nitrogen atoms is in direct combination with three carbon atoms, the formation of trimethylamine might have been predicted. Jn. W.

Glucosamine. A Reply. By Ernst Winterstein (*Ber.*, 1895, **28**, 1372—1374; compare this vol., i, 80).—A reply to E. Gilson's criticisms (this vol., i, 323) on the author's work on the isolation of glucosamine hydrochloride from the decomposition products of "fungus cellulose." J. J. S.

Diazomethane. By Hans v. Pechmann (*Ber.*, 1895, **28**, 1624—1628).—Diazomethane may be used in the preparation of methylic derivatives, addition of CH_2 taking place whilst nitrogen is

evolved. Its action on phenol, for example, is represented by the equation $C_6H_5\cdot OH + CH_2N_2 = C_6H_5\cdot OCH_3 + N_2$ (compare this vol., i, 328). The action takes place at the ordinary temperature, and is thus likely to be useful in determining the constitution of compounds that react in tautomeric forms. It is brought about by mixing an ethereal solution of diazomethane with the substance to be investigated, the latter in alcoholic solution when necessary.

2-Pyridone yields only the oxygen ether, $C_5NH_4\cdot OMe$ [OMe = 2], and hence probably exists in the form $C_5NH_4\cdot OH$ rather than $C_5(NH)H_4{:}O$.

Commercial pyrazolone yields mainly an oxygen-ether, Knorr's 5 : 3 : 1-methoxymethylphenylpyrazole (this vol., i, 397), together with a trace of the nitrogen ether, antipyrine. Pyrazolone itself has therefore probably the constitution $NPh<\begin{matrix}N = CMe\\ |\\ C(OH)\cdot CH\end{matrix}$.

Ethylic acetoacetate yields ethylic *β*-methoxycrotonate, probably the *cis*-modification, for it boils at 186—190° under 725 mm. pressure, about 15° higher than the (probably *trans*-) compound prepared by Enke (Abstr., 1890, 865). It yields the same methoxycrotonic acid when hydrolysed as does Enke's compound; but ethylic acetoacetate only reacts very slowly with diazomethane, and hence probably exists but to a slight extent as $OH\cdot CMe{:}CH\cdot COOEt$, the greater part being $CMeO\cdot CH_2\cdot COOEt$.

Ethylic malonate does not react with diazomethane in ethereal solution at the ordinary temperature. C. F. B.

New Synthesis of Diazomethane. By Eugen Bamberger and Edm. Renauld (*Ber.*, 1895, **28**, 1682—1685).—Diazomethane, which is the anhydride of the hypothetical isodiazomethane hydroxide, $Me\cdot N{:}N\cdot OH$, may be prepared in an analogous manner to isodiazobenzene, which is formed by the action of hydroxylamine on nitrosobenzene (this vol., i, 459). Nitrosomethane is unknown, but the analogous dichloromethylamine, $NMeCl_2$, is readily obtained in quantity by the action of bleaching powder on methylamine hydrochloride; it boils at 58—60°. When heated with water, it explodes violently forming hydrogen cyanide, a similar explosion taking place when a flame is brought near the mouth of a vessel in which the two compounds are warmed.

To prepare diazomethane, dried hydroxylamine hydrochloride is dissolved in methylic alcohol, mixed with the requisite quantity of sodium methoxide also dissolved in methylic alcohol, and a solution of dichloromethylamine in absolute ether gradually added. An ethereal solution of diazomethane distils over, and is condensed in receivers cooled with ice; the solution has all the properties described by v. Pechmann (this vol., i, 328). The yield is not so good as by v. Pechmann's method, but the new synthesis forms a quick and convenient method of obtaining the substance in small quantities.

The reaction by which it is formed is represented by the equation

$$CH_3\cdot NCl_2 + NH_2\cdot OH = 2HCl + CH<\begin{matrix}N\\ ||\\ N\end{matrix} + H_2O.$$

As it is formed by a reaction which yields isodiazobenzene derivatives, the author thinks it probable that this, as well as the aliphatic diazo-derivatives described by Curtius, are also isodiazo-derivatives, the supposition being strengthened by the stability of the compounds, and their inability to form colouring matters with phenols and aromatic bases. H. G. C.

Nitrosopropylacetamide. By Felix Chancel (*Bull. Soc. Chim.*, 1895, [3], **13**, 125—126).—*Nitrosopropylacetamide*, $NAcPr^{\alpha}\cdot NO$, obtained by the action of nitrous acid on propylacetamide, is a mobile, yellowish, or, in thick layers, rose-coloured, liquid, having a pleasant, ethereal odour. Sp. gr. = 1·035 at 15°. It is almost insoluble in water, and at 100°, either alone or in presence of water, is decomposed into nitrogen and propylenic acetate, together with some propylene and acetic acid resulting from the decomposition of the latter. Jn. W.

Action of Thiocarbamide on Ethylic Bromomalonate, Bromolevulinic acid, and Dibromolevulinic acid. By Max Conrad and L. Schmidt (*Annalen*, 1895, **285**, 203—211; compare Tambach, this vol., i, 13).—*Ethylic thiohydantoïncarboxylate*,

$$\begin{matrix}NH{:}C & --- & S\\ | & & \\ NH\cdot CO & & \end{matrix}\!\!>CH\cdot COOEt,$$

is obtained by adding a concentrated aqueous solution of thiocarbamide to ethylic bromomalonate; it is insoluble in ether, but dissolves readily in boiling alcohol, and undergoes decomposition when treated with boiling water. It becomes brown at 165°, and melts evolving gas at 175°; with ferric chloride, the aqueous solution develops a dark-blue coloration, which is destroyed on heating the liquid, and does not reappear at the ordinary temperature. On boiling a solution of ethylic thiohydantoïncarboxylate in hydrochloric acid, carbonic anhydride is liberated and thiohydantoïn is formed, and the same change is effected by sodium hydroxide at ordinary temperatures and also by hot barium hydroxide. Sodium ethoxide gives rise to a gelatinous substance, which probably consists of the sodium compound.

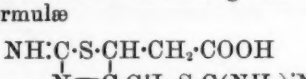
α-Methyl-μ-amidothiazole-β-acetic acid,

$$\begin{matrix}NH{:}C & --- & S\\ | & & \\ N{:}CMe & & \end{matrix}\!\!>CH\cdot CH_2\cdot COOH, \text{ or } \begin{matrix}NH{:}C & --- & S\\ | & & \\ NH\cdot CMe & & \end{matrix}\!\!>C\cdot CH_2\cdot COOH,$$

is prepared by triturating, in contact with water, a mixture of thiocarbamide and bromolevulinic acid in molecular proportion; a solution is obtained, which after 24 hours is neutralised with sodium hydrogen carbonate. It crystallises from water in slender, lustrous prisms, and melts at 259—260°, evolving gas; the aqueous solution has an acid reaction, and decomposes carbonates when heated. The compound dissolves in boiling hydrochloric acid, which, on cooling, deposits the *hydrochloride* in colourless plates; this salt does not yield a precipitate with platinum tetrachloride. The *barium* salt is amorphous, and treatment with excess of hot barium hydroxide effects decomposition,

barium sulphide and barium carbonate being formed; a neutral solution of the barium salt forms a green precipitate with copper acetate, whilst silver nitrate gives rise to a white precipitate which becomes black when heated, owing to the formation of silver sulphide. The *ethylic* salt is obtained by mixing alcoholic solutions of thiocarbamide and ethylic bromolevulinate; it separates from alcohol in small, yellowish crystals, and melts at 123°. The *platinochloride* is obtained by dissolving the ethylic salt in cold hydrochloric acid and treating the solution with platinum tetrachloride; it is a yellow crystalline substance. Ammonia and hot hydrochloric acid hydrolyse the ethylic salt, forming the acid and the hydrochloride respectively.

When a mixture of dibromolevulinic acid and thiocarbamide (2 mols.) is triturated in contact with a small quantity of water, a *compound* is formed having the constitution represented by one of the formulæ



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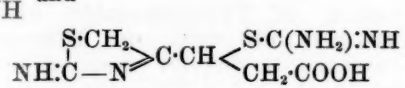


It melts and becomes brown at 175—176°, evolution of gas taking place at this temperature. The formation of this compound is in agreement with the constitutional formula for dibromolevulinic acid put forward by Wolff (Abstr., 1893, i, 689). M. O. F.

Preparation of Diamidoacetone. By Georg Kalischer (*Ber.*, 1895, **28**, 1519—1522).—Diisonitrosoacetone, prepared from acetonedicarboxylic acid, when reduced by means of stannous chloride in hydrochloric acid solution, yields *diamidoacetone stannochloride*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NH_2,2HCl,SnCl_2$, which is crystalline and melts at 203°, after previously blackening. The yield is 66 per cent. of the theoretical. The hydrochloride is readily obtained by the action of hydrogen sulphide on the preceding compound, but its complete purification is difficult on account of its solubility; it crystallises with $1H_2O$, not $1\frac{1}{2}H_2O$, as Rügheimer states. The *picrate*,

$$C_3H_8N_2O2C_6H_3N_3O_7 + H_2O,$$

crystallises in lustrous, long, yellow needles, which char at about 180° without melting. When warmed with Fehling's solution, diamidoacetone hydrochloride gives a dark brown precipitate, which is almost black when dry; it contains about 55 per cent. of copper, and yields water and ammonia when heated. Attempts to prepare dihydroxyacetone by the action of nitrous acid on diamidoacetone hydrochloride were not very successful, as the componnd could not be completely purified, its presence was recognised by the formation of the osazone which melted at about 170°. J. B. T.

Action of Hypochlorous acid on Bisubstituted Acetylene Hydrocarbons. By Al. Faworsky and in part by K. Desbout (*J. pr. Chem.*, 1895, [2], **51**, 533—563).—When hypochlorous acid

(3 per cent.) is added gradually and in small portions to methyl ethyl ketone, both being at 0°, a heavy oil separates. The bulk of this oil distils at 55—58° at 20 mm. pressure, and proves to be *methyl α-dichloropropyl ketone*, $CEtCl_2·COMe$; it is a yellowish liquid, boils at 138° (756 mm.), and has sp. gr. = 1·19519 at 0°. Its constitution is confirmed by the fact that, when treated with hydroxylamine it yields the same dioxime as was obtained by Schramm from isonitrosomethyl ethyl ketone and hydroxylamine ("methylpropylacetoximic acid," Abstr., 1883, 590). The behaviour of this dichloroketone with potassium carbonate has already been described (Abstr., 1893, i, 391). A small fraction of the crude oil from which the dichloroketone is distilled boils between 108° and 112°, and appears to be α-dichlorobutaldehyde.

The reaction between methylpropylacetylene and hypochlorous acid yields *methyl α-dichlorobutyl ketone*, $CPr^{\alpha}Cl_2·COMe$, which is a yellowish liquid, boils at 162—164° (765 mm.), and has a sp. gr. = 1·14695 (at 0°). With hydroxylamine, it yields Schramm's methylpropylglyoxime (Abstr., 1884, 51). This dichloroketone also yields a quinone and two unsaturated acids when heated with a 10 per cent. solution of potassium carbonate (compare Abstr., 1893, i, 391); these are probably diethyldimethylquinone, α-propylacrylic acid, and α-methyl-β-ethylacrylic acid respectively, but none of these could be isolated in a pure condition.

Dimethylacetylene and hypochlorous acid yield *methyl α-dichlorethyl ketone*, $CMeCl_2·COMe$, which boils at 113—114°, and has a sp. gr. = 1·2217 at 0°. Diacetyldioxime was obtained by treating the dichloroketone with hydroxylamine. Démétre-Vladesco has prepared a dichlorinated methyl ethyl ketone (Abstr., 1892, 424) which boils at 165°, and to which he ascribes the formula given above; the authors have attempted to prepare diacetyldioxime from Vladesco's compound, but without success; they therefore conclude that Vladesco's dichloroketone is the symmetrical derivative.

Asymmetrical dichloracetone yields acrylic acid when heated with 10 per cent. potassium carbonate solution, so that it may now be regarded as established that, by this treatment, 1 : 1-dichloro-2-ketones of the type $R'·CO·CHCl_2$ yield acids of the type $R''{:}CH·COOH$, whilst 3 : 3-dicloro-2-ketones of the type $R'·CCl_2·CO·CH_3$ yield acids of the type $R''{:}CR'·COOH$.

From ethylpropylacetylene and hypochlorous acid, a dichlorinated ketone is obtained which yields a dioxime (m. p. 129°), and must, therefore, contain the group $CO·CCl_2$, but whether it be

$$CH_3·CH_2·CH_2·CCl_2·COEt$$

or $CH_3·CH_2·CH_2·CO·CCl_2Et$ remains unsettled; it boils about 174°, and its sp. gr. at 0° is 1·1176. This dichloroketone also yields substituted acrylic acids when heated with 10 per cent. potassium carbonate, and since it contains an alkyl group in place of the methyl group of the foregoing ketones, it may be claimed that in this paper it is established that hydrocarbons of the type R·C:CH yield, when treated with hypochlorous acid, dichloroketones of the type

$$R·CO·CCl_2·r,$$

and that these, on treatment with potassium carbonate solution, yield acids of the type R″:Cr′·COOH or r″·cR′·COOH. A. G. B.

Constitution of Isonitrosoketones. By GEORG KALISCHER (*Ber.*, 1895, **28**, 1513—1519).—The reduction products of isonitrosopropyl methyl ketone, COMe·CEt:NOH, have been previously described by Gabriel and his students (Abstr., 1893, i, 734; 1894, i, 355). The compounds are indistinguishable in appearance from those obtained by the reduction of Claisen and Manasse's isonitrosoketone, COPr·CH:NOH (Abstr., 1889, 584), and the melting points are shown to be practically identical. The former yields dimethyldiethylpyrazine, if the formula of the latter is correct it should yield dipropylpyrazine. Dimethyldiethylpyrazine, when completely oxidised with potassium permanganate, yields a tetrabasic acid which could not be purified; when more cautiously oxidised, dimethylpyrazinedicarboxylic acid, $N<^{CMe\cdot C(COOH)}_{C(COOH)\cdot CMe}>N$, is formed; it has been previously prepared by Weengel from ethylic isonitrosoacetoacetate. As dipropylpyrazine could not yield this acid, the isonitrosoketones must be identical, and have the formula COMe·CEt:NOH. By the action of amylic nitrite and hydrochloric acid on ethyl methyl ketone, an isonitroso-derivative is formed which melts at 74°, and crystallises in slender, colourless needles; the compound from ethylic methylacetoacetate melts at 73—75°; these are also doubtless identical, and have the formula COMe·CMe:NOH. Fileti and Ponzio's investigation of isonitrosononyl methyl ketone, $COMe\cdot C(C_8H_{17}):NOH$, confirms this, and it appears to be a rule that by the action of amylic nitrite and hydrochloric acid on ketones of the formula $COMe\cdot CH_2R$, the methylene, and not the methyl, group reacts.

J. B. T.

Diacetylacetone. By FRANZ FEIST and HANS BELART (*Ber.*, 1895, **28**, 1817—1829).—Diacetylacetone, $CO(CH_2\cdot CMeO)_2$, is best prepared by treating the compound $C_7H_9O_3Cl + 3H_2O$ (Collie, Trans., 1891, 619) with concentrated baryta water, adding to the yellow barium xantho-salt (Abstr., 1889, 957), thus obtained, cold, moderately concentrated hydrochloric acid, and extracting with ether. It reacts with hydroxylamine much in the same way as with phenylhydrazine (*Annalen*, **257**, 278, 292).

Diacetylacetonedioxime, $C_7H_{10}O(NOH)_2$, crystallises in needles, and melts at 68·5°; the *hydrochloride* in white needles, which melt at 132°. The latter is converted by moderately concentrated aqueous soda into the *anhydride* of the dioxime, $C_7H_{10}N_2O_2$; this crystallises in yellow needles, and melts, decomposing with a slight explosion, at 242·5°; it may also be obtained by heating the dioxime at 120—125° in a test-tube. The action of hydrogen cyanide on diacetylacetone gave no definite result. Phosphorus pentachloride removes water, dimethylpyrone being formed. By treating diacetylacetone (1 mol.) with acetic chloride (rather more than 2 mols.) in the cold, white plates, melting at 44°, were obtained; these probably consist of the *diacetyl derivative*. By heating a mixture of diacetylacetone (1 mol.), benzoic chloride (2 mols.), and sodium ethoxide (2 mols.), a *di-*

benzoyl derivative was obtained; it crystallises in yellow needles, melts at 55°, and dissolves in alkalis. When a crude sample of this dibenzoyl derivative was distilled, acetic acid, ethylic benzoate, benzoic chloride, and benzoylacetone were obtained, together with a substance, $C_{14}H_{14}O_3$, which crystallises in white needles. Diazobenzene chloride yields, with diacetylacetone, a compound which, probably, has the constitution $CO[CH(N_2Ph)\cdot CO\cdot CH\cdot N_2Ph]_2$; it crystallises in dark reddish-brown needles, and melts at 152°. When diacetylacetone is boiled with ethylic acetoacetate in benzene solution, in the presence of solid sodium ethoxide, a small quantity of a neutral substance, $C_{13}H_{14}O_3$, is obtained, together with an acid, $C_{11}H_{14}O_5$; they both crystallise in yellow needles, and melt respectively at 170° and 197°. The second substance is the carboxylic acid of the first, and is also formed, although in smaller amount, when ethylic acetate is used instead of the acetoacetate; it is possibly an ethoxy-derivative formed by the substitution of ethyl for one of the hydroxyl hydrogens in the trihydroxymethylnaphthoic acid,

$COOH\cdot C_{10}H_3Me(OH)_3$ [Me : $(OH)_3$: COOH = 1 : 4 : 4′ : 2′ : 3′].

C. F. B.

Conversion of Ketones into α-Diketones. By Michele Fileti and Giacomo Ponzio (*J. pr. Chem.*, 1895, [2], **51**, 498—510, and *Gazzetta*, 1895, **25**, i, 233—245; compare this vol., i, 15.)—By the oxidation of methyl ethyl ketone with nitric acid (sp. gr., 1·38), dimethyl diketone, acetic acid, ammonia and dinitroethane are produced; methyl propyl ketone yields methyl ethyl diketone and dinitropropane, methyl butyl ketone gives methyl propyl diketone and dinitrobutane, whilst methyl hexyl ketone yields methyl amyl diketone, dinitrohexane, and caproic acid. Directions are given for the best method of conducting the oxidation, and the dioximes of the diketones, obtained incidentally as a means of isolating the diketones, are described. *Methyl amyl diketone dioxime*, which crystallises in lustrous prisms and melts at 170°, is the only one of these which has not been previously prepared. A. G. B.

Formation of Ethereal Salts. By Rudolf Wegscheider (*Ber.*, 1895, **28**, 1468—1474; compare this vol., i, 420).—The author discusses the difference between the views held by Meyer on this question and those previously put forward by himself. He considers that etherification by hydrogen chloride and an alcohol, and hydrolysis are both preceded by the formation of additive compounds, whilst etherification by the action of an alkylic iodide and a silver salt is effected by a direct exchange between the atom of the metal and the alkyl group. Meyer on the other hand refers the difference in the behaviour of the free acid and the silver salt to the different amount of space occupied by the atoms of silver and hydrogen. In considering the effect of neighbouring groups, the author considers that the important point is the volume of the element or group in question, whilst Meyer attaches most importance to its weight. A. H.

An Octylic (Ethylmethylvaleric or Ethylisobutylacetic) Acid. By Philippe A. Guye and J. Jeanprêtre (*Bull. Soc. Chim.*, 1895, [3], **13**, 182—185).—*Ethylic ethylisobutylacetate*,

$$CHMe_2\cdot CH_2\cdot CHEt\cdot COOEt,$$

prepared from ethylic acetoacetate by the well known synthetical method, boils at 230—233°; sp. gr. = 0·954 at 15°. The free *acid* boils at 219—220° (729 mm.); sp. gr. = 0·906 at 15°. The *chloride* boils at 165—172°. The *anilide* crystallises in characteristic, thin, flat needles, and melts at 77—78°; it is soluble in the usual menstrua. The intermediate product, *ethylic isobutylacetoacetate*,

$$CHMe_2\cdot CH_2\cdot CHAc\cdot COOEt,$$

boils at 215—220°. *Ethylisobutylbromacetic chloride*,

$$CHMe_2\cdot CH_2\cdot CEtBr\cdot COCl,$$

prepared by brominating the above chloride, has a sharp, disagreeable odour, and boils at 220—240°. An additive product with 1 mol. of bromine appears to be formed in the first instance, as hydrogen bromide is not disengaged at 100°, even after 2 or 3 hours heating, although the colour of the bromine disappears. At a higher temperature, hydrogen bromide is freely evolved, and the bromacetic chloride distils over. *Ethylic ethylisobutylbromacetate*, prepared from the chloride in the usual manner, boils at 160—165° (80—100 mm.).

Jn. W.

Triricinolein. By Paul Juillard (*Bull. Soc. Chim.*, 1895, [3], **13**, 240—246).—When triricinoleïn is boiled with toluene, either alone or in presence of zinc chloride, it condenses to various ethers, such as that represented by the formula,

$$[(OH\cdot C_{17}H_{32}\cdot COO)_2C_3H_5\cdot C_{17}H_{32}\cdot CO]_2O,$$

which differ from it in their sparing solubility in alcohol and light petroleum. On account of the slight differences in their composition, their formulæ were established by cryoscopic determinations, both on the substances themselves, and on the mixtures of acids, such as ricinoleïc and diricinic acids resulting from them by hydrolysis. They are all oily liquids.

Triricinoleïn can be synthetised by heating ricinoleïc acid with glycerol at 120—230°, unchanged glycerol and acid being dissolved out with water and light petroleum. The product is identical in every respect with that from castor oil. When, however, the parent substances are heated together under the conditions followed by Berthelot in synthetising the palmitins, condensation products of mono- and di-ricinoleïn are formed, the simplest of which is isomeric with triricinoleïn, and has the formula,

$$OH\cdot C_{17}H_{32}\cdot COO\cdot C_{17}H_{32}\cdot COO\cdot C_3H_5(C_{17}H_{32}\cdot COOH)_2.$$

The ricinoleïc acid prepared by Krafft's method is not pure. The pure acid is best obtained from its barium salt after repeated recrystallisation of the latter from alcohol. It melts at 4—5°.

Jn. W.

Natural Dihydroxystearic Acid. By Paul Juillard (*Bull. Soc. Chim.*, 1895, [3], **13**, 238—240).—Castor oil contains, besides ricinoleïc and stearic acids, a dihydroxystearic acid isomeric with that

from Turkey red oil (this vol., i, 82), the crude ricinoleïc acid obtained by hydrolysis of the oil depositing, when kept for some days at a temperature below 12°, a white, crystalline magma of a mixture of stearic acid and the new acid. After purification by pressure, and crystallisation from alcohol, the stearic acid is dissolved out with toluene, and the hydroxy-acid crystallised from boiling alcohol. The yield is about 1 per cent.

Dihydroxystearic acid, $C_{18}H_{36}O_4$, the molecular weight of which was determined by the cryoscopic method, is insoluble in ether, light petroleum and benzene, only sparingly soluble in toluene, but freely in boiling alcohol and acetic acid. It melts at 141—143°. It does not absorb iodine, and is reduced to ordinary stearic acid by hydriodic acid and red phosphorus at 180°, or by zinc and acetic acid. It is a monobasic acid. The *potassium*, *sodium*, and *barium* salts are normal. The *methylic* salt crystallises in plates, and melts at 106—108°; the *ethylic* salt resembles it and melts at 104—106°.

When heated in a stream of dry carbonic anhydride at 220° for eight hours, dihydroxystearic acid is converted into a viscous, feebly acid oil, soluble in ether and insoluble in alcohol; probably a *condensation product* analogous to the ricinoricinic acids; the molecular weight, determined by the cryoscopic method, points to the condensation of 4 mols. of the original acid with elimination of 3 mols. of water. By prolonged boiling with alcoholic potash, the product is gradually hydrolysed with formation of the original acid. A second oily condensation product, obtained by heating the dihydroxy-acid with concentrated hydrochloric acid at 180°, or with zinc chloride in toluene solution, is probably a mixture of a dibasic, *dihydroxy-acid*, $[C_{17}H_{33}(OH)\cdot COOH]_2O$, and the corresponding monobasic *lactone*; it is soluble in the usual organic menstrua, and has a molecular weight, as determined by the cryoscopic method, of 507. JN. W.

Maize Meal Fat. By F. ROKITIANSKI (*Chem. Centr.*, 1895, i, 22; from *Pharm. Zeit. f. Russland*, 1894, **33**, 712—713).—An aromatic, yellow, neutral oil, of density 0·836, is extracted by light petroleum from the small yellow Italian maize grown in Southern Russia; it gives the elaïdin reaction and has a Hübl's iodine number of 75·8 and a Reichert-Meissl number of 0·87. Formic acid was detected, and capronic, caprylic and capric acids also are probably present; the solid fatty acids contain oleïc acid and hydroxy-acids, as is shown by their iodine number (97·8), their lead salts, and their behaviour on acetylation, and yield a mixture of ethylic salts boiling at 240—242°. On oxidising the acid regenerated from this salt, a *tetrahydroxystearic* acid melting at 168—170°, and probably also a *dihydroxystearic acid*, are obtained. The readiness with which maize meal becomes rancid is probably due to the presence of linoleïc acid.
W. J. P.

Acetylacetone. Ethylic Acetoacetate. By RICHARD S. CURTISS (*Amer. Chem. J.*, 1895, **17**, 435—443).—The neutral compound obtained by Nef from the reaction between silver acetylacetone and ethylic iodide (Abstr., 1894, i, 31) is shown to be *α-acetyl-β-ethoxypropylene*; it is a fragrant oil which becomes light green on standing.

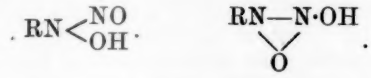
The α-ethylacetylacetone formed at the same time (*loc. cit.*) yields a *copper* derivative, $C_{14}H_{22}O_4Cu$, when shaken with an aqueous solution of copper acetate; it is insoluble in water, but dissolves in most hot organic solvents and in cold chloroform, and crystallises in long, silky, greyish-green needles which become brown at 205° and melt at 210—212°.

Claisen (this vol., i, 62) states that, among other points of difference which he observes between the behaviour of hydroxymethylene compounds and that of ethylic acetoacetate, the hydroxymethylene compounds are converted into ethylic salts by the action of hydrochloric acid and alcohol. The author shows that ethylic acetoacetate is converted by alcohol, alone or in the presence of hydrogen chloride, into ethylic β-ethoxycrotonate; he thus disposes of Claisen's point of difference.

When ethylic β-ethoxycrotonate is treated with bromine (1 mol.) in carbon tetrachloride at −10°, the ethylic salts of α- and γ-bromo-β-ethoxycrotonic acids are formed, together with those of α- and γ-bromacetoacetic acids.

Hantzsch and Epprecht (Abstr., 1894, i, 171) have attempted to throw doubt on Nef's experiments, which showed that Duisberg's ethylic bromacetoacetate is a mixture of the ethylic salts of α- and γ-bromacetoacetic acids (Abstr., 1892, 143). The author has re-examined Duisberg's product, and has isolated the copper salt of ethylic α-bromacetoacetate from it. A. G. B.

Isonitramine and Oxazo-derivatives of Fatty acids. By WILHELM TRAUBE (*Ber.*, 1895, **28**, 1785—1797; compare Abstr., 1894, i, 400, this vol., i, 124).—The isonitramine derivatives of ethylic acetoacetate, previously described by the author, are readily hydrolysed by alkalis with simultaneous elimination of the acetyl group and formation of the corresponding isonitramine fatty acid. These form crystalline salts, but, with the exception of isonitraminephenylpropionic acid, none of the free acids could be obtained in the crystalline condition. On reduction in acid solution, these compounds yield the corresponding amido-acids, whilst in alkaline solution they are converted into hydrazines; hence the two nitrogen atoms must be directly connected together, and one must also be directly combined with carbon. Either of the following constitutional formulæ fulfils these conditions equally well:—



Ethylic isonitramineacetoacetate is best prepared by passing nitric oxide into an alcoholic solution of ethylic acetoacetate (1 mol.) and sodium ethoxide (1 mol.), and, after complete saturation, adding another mol. of sodium ethoxide. The precipitated sodium salt is very susceptible to the action of acids, 70—80 per cent. of the nitrogen being evolved in the free state, whilst acetic and oxalic acids are formed together with ethylic isonitrosoacetoacetate. On treatment with phenylhydrazine, it yields the *hydrazone of ethylic acetoglycollate*,

$N_2HPh{:}CMe{\cdot}CH(OH){\cdot}COOEt$, which crystallises in rhombic plates melting at 102°. For the preparation of *isonitramineacetic acid*, $HO_2N_2{\cdot}CH_2{\cdot}COOH$, the crude solution obtained by the action of nitric oxide on ethylic sodacetoacetate is mixed with the theoretical quantity of soda, and warmed until all the alcohol is driven off; the acid is then precipitated as the lead salt, which is crystalline and insoluble in water. The *calcium* salt, $C_2H_2N_2O_4Ca + 2H_2O$, crystallises in well developed prisms which do not lose water at 180°. The *ammonium* salt, which, like all the ammonium salts of these acids, only contains 1 mol. of ammonia, crystallises in colourless plates which melt at 166—168° and then decompose without explosion; the *barium* salt is granular, and the *silver* salt forms concentric aggregates of needles. The free acid is stable only in solution. *Isonitraminepropionic acid*, $HO_2N_2{\cdot}CHMe{\cdot}COOH$, obtained in the same manner from ethylic methylacetoacetate, closely resembles the foregoing compound; its *lead* salt, $C_3H_4N_2O_4Pb$, is crystalline, and insoluble in water and dilute acetic acid. *Isonitraminebutyric acid*, $HO_2N_2{\cdot}CHEt{\cdot}COOH$, prepared from ethylic ethylacetoacetate, is also only known in solution; the *lead* salt is a crystalline, explosive powder; the *barium* salt, $C_4H_6N_2O_4Ba$, forms crystalline crusts, and the *ammonium* salt concentric aggregates of broad, colourless needles melting and decomposing at 156—159°. Salts of *isonitraminevaleric acid* have also been prepared. *Isonitraminephenylpropionic acid*, $HO_2N_2{\cdot}CH(CH_2Ph){\cdot}COOH$, differs from the foregoing compounds, inasmuch as it has been obtained in the crystalline state. It is prepared from ethylic benzylacetoacetate, and forms large, yellowish crystals containing $2H_2O$ which are rapidly removed if it is kept over sulphuric acid. It melts at 72°, and gives Liebermann's reaction; its *ammonium* salt crystallises in plates and melts at 179°.

Ethylic malonate, in presence of sodium ethoxide, absorbs nitric oxide more readily than ethylic acetoacetate does; the product on boiling with the requisite quantity of soda yields a sodium salt having the composition $N_2OC(COONa)_2 + 2H_2O$, which forms lustrous needles and loses its water of crystallisation at 130—140°. The *barium* salt, $N_2OC(COO)_2Ba$, crystallises in lustrous plates and loses its water of crystallisation at 170°; the *calcium* salt forms prisms, and the *lead* salt a curdy precipitate which gradually becomes crystalline. All the salts are explosive, and the free acid could not be obtained crystalline. This acid contains the elements of 1 mol. water less than the isonitramine malonic acid $HO_2N_2{\cdot}CH(COOH)_2$, whose formation was expected, and it has, therefore, probably the constitution $ON_2{:}C(COOH)_2$, and the author proposes for it the name *oxazomalonic acid*. Another possible formula is $\begin{matrix} O{-}CO \\ | \\ O{-}N_2 \end{matrix}\!>\!CMe{\cdot}COOMe$, but it is very improbable that a lactone-like substance of this constitution would be formed by the action of boiling alkalis. In addition to oxazomalonic acid, small quantities of isonitramineacetic acid are also formed, and in the case of the substituted ethylic malonates only the isonitramine fatty acids are obtained, no compounds analogous to oxazomalonic acid having yet been prepared.

Benzylic cyanide is acted on by nitric oxide in presence of sodium

ethoxide forming the very unstable *diisonitraminebenzylic cyanide*, $CPh(N_2O_2H)_2CN$, which forms a snow-white, crystalline powder. Its *barium* salt, $C_8H_5N_5O_4Ba$, is crystalline, and almost insoluble in water, and, like the other salts, is decomposed by acetic acid with formation of isonitrosobenzyl cyanide. H. G. C.

Derivatives of Galactonic acid. By EMIL KOHN (*Monatsh.*, 1895, **16**, 333—343; compare Skraup, Abstr., 1894, i, 15).—When hydrogen chloride is passed through calcium galactate suspended in alcohol, the liquid at first becomes clear, but later a substance of the composition $(C_6H_{11}O_7Et)_2CaCl_2$, separates as a gelatinous mass which soon becomes crystalline. The free *ethyl derivative*, on account of its instability, could not be isolated from this compound, but the *pentacetyl derivative*, $CH_2(OAc)\cdot[CH\cdot OAc]_4\cdot COOEt$, was formed on acetylation with acetic chloride, or still better, with acetic anhydride. It is crystalline, melts at 101—102°, and with ammonia yields the *amide* of *galactonic acid*, $C_5H_{11}O_5\cdot CONH_2$, which at 172—173° melts with decomposition and evolution of gas. The *anilide* of *galactonic acid*, $C_5H_{11}O_5\cdot CONHPh$, crystallises from alcohol in bright scales and melts at 210°. G. T. M.

Separation and Identification of Alkylated Succinic and Glutaric acids. By KARL AUWERS (*Annalen*, 1895, **285**, 212—229).—Two general methods for the separation of substituted succinic and glutaric acids are described, namely: (1) treatment with acetic chloride, which converts some acids of this type into the anhydride, leaving others unchanged; (2) distillation in an atmosphere of steam. Reference must be made to the original paper for details of the separation, which are influenced by the composition of the mixture.

Identification of the various acids depends on their more important characteristics; for instance, melting point, volatility, temperature at which elimination of water takes place, crystalline form, solubility, behaviour towards hot hydrochloric acid, electrical conductivity, and behaviour of the anhydrides towards bases. The last-named method of characterisation is carried out by preparing a solution of the anhydride in benzene and treating it with a molecular proportion of an aromatic base dissolved in the same medium; in this way, an anilic acid is obtained which, if derived from a glutaric acid, melts without decomposition, but becomes converted into an anil through elimination of water if the original anhydride is of the succinic type. The anils and anilic acids, which find useful application in this way, are described in the following abstract. M. O. F.

Anilic acids and Anils of Alkylated Succinic and Glutaric acids. By KARL AUWERS, A. OSWALD, and JOCELYN F. THORPE (*Annalen*, 1895, **285**, 229—239; compare this vol., i, 209).—The general method of preparing the anilic acids consists in mixing benzene solutions of the anhydride and a base; the anils are obtained from the anilic acids by heating them at the melting point, or in the case of those derived from glutaric acid, heating them for a

few minutes at the boiling point under reduced or atmospheric pressure.

The following derivatives have been prepared from dimethylsuccinic acid (high melting point). The *anilic acid* melting at 169°; the *anil* at 126—127°; the *paratolilic acid* at 198°; the *paratolil* at 120°; the *β-naphthilic acid* at 209°; and the *β-naphthil* at 200°.

The anil of dimethylsuccinic acid (low melting point) has been already described (Bischoff and Voit, *Ber.*, 1890, **23**, 643). The *anilic acid* melts at 135—136°; the *paratolilic acid* at 164—165°; the *paratolil* at 153°; the *β-naphthilic acid* at 140°; and the *β-naphthil* at 220°. M. O. F.

Trimethylsuccinic acid and the Symmetrical Dimethylglutaric acids. By KARL AUWERS (*Annalen*, 1895, **285**, 241—284; compare this vol., i, 209; also Bone and Perkin, Trans., 1895, 416).—A preliminary notice of the work has already appeared (*loc. cit.*), and the author's conclusion that trimethylsuccinic acid occurs in one form only, melting at 147°, has been confirmed by Bone and Perkin (*loc. cit.*). The present paper treats the subject in a more detailed manner, and summarises the experimental evidence to which the two following abstracts have reference.

The fumaroïd dimethylglutaric acid yields the anhydride less readily than the maleïnoid form, and on this circumstance the author bases an argument in favour of v. Baeyer's explanation of the isomerism of dialkylated succinic acids and similar compounds; a view is also put forward which accounts for the preponderance of the maleïnoid modification in the mixture of acids obtained from ethylic sodio-α-cyanopropionate and methylenic iodide.

Attention has already been drawn by v. Baeyer to the similarity between hexahydro-derivatives of the benzenedicarboxylic acids and the aliphatic acids containing the same number of carbon atoms between the carboxyl groups (Abstr., 1893, i, 714); the author shows that the resemblance between the symmetrical dimethylglutaric acids and the hexahydroisophthalic acids is not maintained in every particular. M. O. F.

Sources of Trimethylsuccinic acid. By KARL AUWERS and A. OSWALD (*Annalen*, 1895, **285**, 283—309; compare foregoing abstract, also this vol., i, 209, and Trans., 1895, 416).—The paper contains a description of the various methods of obtaining trimethylsuccinic acid. The *lead* and *copper* salts are crystalline, and contain $1H_2O$; the *imide* crystallises in lustrous needles, and melts at 121°. M. O. F.

Symmetrical αα-Dimethylglutaric acids. By KARL AUWERS and JOCELYN F. THORPE (*Annalen*, 1895, **285**, 310—339; compare this vol., i, 209).—The authors describe methods for the preparation of the symmetrical dimethylglutaric acids; the main facts have already appeared (*loc. cit.*).

The fumaroïd acid crystallises in long prisms belonging to the monosymmetric system, $a : b : c = 0{\cdot}4409 : 1 : 0{\cdot}295$; $\beta = 94° 16' 30''$. The maleïnoid modification forms crystals belonging to the asym-

metric system, $a : b : c = 0{\cdot}4688 : 1 : —$; $\alpha = 107° 49' 30''$, $\beta = 114° 18'$, $\gamma = 74° 55' 30''$. The anhydride of these acids forms monosymmetric crystals, $a : b : c = 0{\cdot}92547 : 1 : —$; $\beta = 91° 21' 35''$.

M. O. F.

Racemism. By Leo Marchlewski (*Ber.*, 1895, **28**, 1611—1612).—The author points out that he drew attention to the fact that racemic acid in 10—14 per cent. solution has a smaller specific volume than tartaric acid (Abstr., 1892, 964), before Liebisch did, whose work is referred to by Wallach (*Annalen*, **286**, 134) in this connection.

A. H.

Ethylic Oxalosuccinate. By Wilhelm Wislicenus and Max Nassauer (*Annalen*, 1895, **285**, 1—10; compare Abstr., 1894, i, 323).—Specimens of ethylic oxalosuccinate which have been distilled, invariably contain traces of ethylic ethanetricarboxylate owing to elimination of carbonic oxide (*loc. cit.*); a pure product may be obtained, however, by using potassium carbonate in the manner already described, without submitting the oil to distillation; and when prepared in this way, ethylic oxalosuccinate is almost colourless and odourless.

Unlike the ethylic salts of β-ketonic acids, ethylic oxalosuccinate does not yield a ketone or ketonic acid on hydrolysis; when boiled with dilute sulphuric acid, it yields succinic acid, carbonic anhydride, and oxalic acid, the last-named product being further decomposed into carbonic oxide and formic acid. Aqueous potash and baryta also resolve ethylic oxalosuccinate into oxalic and succinic acids, and the action of water at 150° for six hours effects the same result, the oxalic acid undergoing decomposition into carbonic anhydride and formic acid.

The *ethylic* salt of isocitric acid,

$$COOEt{\cdot}CH_2{\cdot}CH(COOEt){\cdot}CH(OH){\cdot}COOEt,$$

(Fittig and Miller, Abstr., 1890, 587), is obtained by reducing ethylic oxalosuccinate with sodium amalgam; it is a colourless, odourless and viscous oil, which boils at 149—150° under a pressure of 14 mm. The *sodium* salt, which is produced at the same time, is extremely soluble in water.

M. O. F.

Ethylic Dioxalosuccinate. By Wilhelm Wislicenus and August Boeckler (*Annalen*, 1895, **285**, 11—34).—*Ethylic dioxalosuccinate*, $COOEt{\cdot}CO{\cdot}CH(COOEt){\cdot}CH(COOEt){\cdot}CO{\cdot}COOEt$, is obtained by the action of sodium ethoxide on a mixture of ethylic oxalate and ethylic succinate dissolved in ether; after several days, the ethereal liquid is agitated with water, and on acidifying the aqueous extract, ethylic dioxalosuccinate is obtained as an oil. The salt combines with phenylhydrazine, hydroxylamine, and ammonia; the alcoholic solution develops a deep reddish-brown coloration with ferric chloride. Carbonic oxide is eliminated from ethylic dioxalosuccinate under the influence of heat, and ethylic ethanetetracarboxylate is formed. The *disodium* salt is a yellow, hygroscopic substance, which dissolves very readily in water; the aqueous solution is alkaline, and reduces copper acetate and mercuric chloride when

gently heated, an intense red coloration being developed in the case of the latter. When the solution of the disodium salt in cold water is neutralised with dilute sulphuric acid, and allowed to remain for several hours at the ordinary temperature, a yellow, crystalline precipitate is formed, consisting of the *sodium* salt of the lactone of ethylic dioxalosuccinate; the warm, aqueous solution reduces mercuric chloride, copper acetate, and Fehling's solution, a red coloration being developed with the mercuric salt. The *lactone* of ethylic dioxalosuccinate, $\begin{matrix}\mathrm{COOEt{\cdot}C{:}C(COOEt)}\\ \mathrm{COOEt{\cdot}CO{\cdot}CH}\text{——}\mathrm{CO}\end{matrix}\!>\!O$, is obtained by adding dilute sulphuric acid to an aqueous solution of the sodium salt; it crystallises from alcohol in lustrous needles, and melts at 89—90°. The lactone is acid in character, and with alkalis, alkali carbonates, or sodium acetate, yields solutions from which it is thrown down by sulphuric acid. The alcoholic solution develops a reddish-brown coloration with ferric chloride, and when copper acetate or mercuric chloride is warmed with the solution in aqueous sodium acetate, the metallic salt is reduced. The lactone is decomposed by hot aqueous sodium hydroxide, yielding oxalic and succinic acids; when the ethereal solution is treated with sodium (1 mol.) dissolved in alcohol, the sodium salt is formed, whilst the disodium salt of ethylic dioxalosuccinate is produced if twice this proportion of sodium is employed. The *ammonium* salt of the lactone crystallises in colourless leaflets, and melts at 160°, gas being evolved at this temperature; at 165° water is eliminated, and a *compound* is formed which melts at 220—227°, and when heated with soda-lime yields a vapour which gives the pyrroline reaction. The *phenylhydrazone*, $\mathrm{COOEt{\cdot}C(N_2HPh){\cdot}CH(COOEt){\cdot}CH(COOH){\cdot}C(N_2HPh){\cdot}COOEt}$, is obtained by adding phenylhydrazine (2—3 mols.) dissolved in glacial acetic acid, to an alcoholic solution of the lactone; it forms small, colourless crystals, and melts at 138°. It dissolves in aqueous sodium hydroxide, and ferric chloride develops an intense violet coloration with the solution in concentrated sulphuric acid.

When the lactone of ethylic dioxalosuccinate is hydrolysed with aqueous soda (2 mols.), the *disodium* salt of the acid lactone of ethylic dioxalosuccinate, $\begin{matrix}\mathrm{COOEt{\cdot}C{:}C(COONa)}\\ \mathrm{COOEt{\cdot}C(ONa){:}C}\text{———}\mathrm{CO}\end{matrix}\!>\!O$, is formed; it is also produced by boiling the alcoholic solution of the disodium salt of ethylic dioxalosuccinate, or on allowing the aqueous solution to remain for several hours at the ordinary temperature. The salt is pale yellow, and insoluble in alcohol, but dissolves readily in water; the aqueous solution is neutral, and yields a white precipitate with solutions of lead acetate and calcium chloride. Barium chloride gives rise to a crystalline precipitate when gently heated; phenylhydrazine acetate produces a yellow, flocculent precipitate, and copper acetate is reduced on application of heat. Mercuric chloride is likewise reduced, the liquid becoming reddish-yellow, the colour being more intense if the solution of the sodium salt is previously heated with aqueous soda.

The *acid lactone* of ethylic dioxalosuccinate,

$$\begin{matrix}\mathrm{COOEt{\cdot}C{:}C(COOH)}\\ \mathrm{COOEt{\cdot}CO{\cdot}CH\text{——}CO}\end{matrix}\!\!>\!\mathrm{O},$$

is prepared from the foregoing disodium salt by treating it with acid, and from the disodium salt of ethylic dioxalosuccinate, by allowing the aqueous solution to become neutral spontaneously, and extracting with ether after the addition of acid. It dissolves readily in water, alcohol, and ether, and crystallises from benzene or chloroform in slender, colourless needles; at 170—171° it melts and evolves gas. The alcoholic solution develops a deep, reddish-brown coloration with ferric chloride, and yields an oil with phenylhydrazine; in its behaviour towards other reagents, it resembles the sodium salt. Boiling aqueous alkalis decompose it into oxalic and succinic acids.

Diethylic dioxalosuccinate,

$$\mathrm{COOEt{\cdot}CO{\cdot}CH(COOH){\cdot}CH(COOEt){\cdot}CO{\cdot}COOH + 3H_2O},$$

is obtained by the action of cold aqueous soda on the disodium salt of the foregoing acid lactone. It separates from hot water in small, lustrous, rhombic crystals, and melts at 90—92°. It reduces copper acetate and Fehling's solution, and in presence of sodium acetate mercuric chloride is also reduced, an intense, blood-red coloration being developed. Ferric chloride does not produce any coloration in the alcoholic solution. The *phenylhydrazone* melts at 160—165°, and the sulphuric acid solution develops a deep violet coloration with ferric chloride. The *barium* salt, $C_{12}H_{12}O_{10}Ba + H_2O$, is crystalline. Cold alkalis have no further hydrolytic action on diethylic dioxalosuccinate, which is resolved, however, by hot solutions into oxalic and succinic acids. Elimination of water takes place when diethylic dioxalosuccinate is heated at 120°, the acid lactone (m. p. 170—171°) being formed. M. O. F.

Action of Hydrazines on Ethylic Ethanetetracarboxylate. By A. Salomon and E. Pohl (*Ber.*, 1895, **28**, 1722—1724).—By the interaction of hydrazine and ethylic ethanetetracarboxylate in dilute alcoholic solution, the dihydrazide, $\begin{matrix}\mathrm{NH{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}NH}\end{matrix}$, is formed; this does not crystallise, reduces silver and copper solutions, yields a dark green oxidation product with ferric chloride, dissolves in dilute ammonia, is decomposed by hydrochloric acid, liberates carbonic anhydride from carbonates, and, with concentrated ammonia, yields a reddish-brown compound, which has not yet been investigated. The *barium* and *calcium* salts contain 1 and $2H_2O$ respectively, both are at first colourless, but the latter rapidly turns blue. Phenylhydrazine and paratolylhydrazine yield corresponding compounds,

$$\mathrm{(NHR{\cdot}NH{\cdot}CO)_2CH{\cdot}CH(CO{\cdot}NH{\cdot}NHR)_2},$$

which could not be recrystallised. J. B. T.

Ortho-Substitution Products in the Thiophen Series. By K. Keiser (*Ber.*, 1895, **28**, 1804—1807).—The starting point for the preparation of these derivatives was dimethylthiophen, obtained from

coal-tar xylene. When the dibromo-derivative is mixed with acetic chloride in light petroleum solution and aluminium chloride added, *monobromacetylmethylthiophen*, $C_4SHMeBrAc$, melting at 77°, is formed. When acetyldimethylthiophen, in carbon bisulphide solution, is treated with the theoretical quantity of bromine in cooled aqueous solution, a *monobromo-derivative* is formed, the bromine having entered the ring; this compound melts at 78°. In the same way, acetothienon can be made to yield its monobromo-derivative.

Benzoyldimethylthiophen, C_4SHMe_2Bz, was prepared by the action of benzoic chloride on dimethylthiophen; it melts at 56°, and yields a *monobromo-derivative*, which melts at 78°, and forms a colourless *oxime;* this oxime does not yield an indoxazen. C. F. B.

Dimethylthiophen (Thioxen). By MORITZ KITT (*Ber.*, 1895, **28**, 1807—1814).—The dimethylthiophen prepared by Paal (Abstr., 1885, 1205) from phosphorus pentasulphide and acetonylacetone, $CMeO{\cdot}CH_2{\cdot}CH_2{\cdot}CMeO$, must obviously have the constitution, $C_4SH_2Me_2$ [$Me_2 = 2:5$]. It has been generally thought to be identical with that from coal-tar, but the author has prepared various derivatives of it, and compared them with the corresponding derivatives of coal-tar dimethylthiophen prepared by himself, Keiser (preceding abstract) and Zelinski (Abstr., 1888, 939). These were found to differ in melting point and in other respects; hence coal-tar thioxen cannot have the 2:5-constitution, but must have one of the three isomeric formulæ.

2:3:5-*Dimethylthienyl phenyl ketone*, $C_4SHMe_2{\cdot}COPh$, prepared by the action of benzoic chloride on synthetical 2:5-dimethylthiophen, melts at 44—45°; Keiser's preparation, from coal-tar dimethylthiophen, melted at 50—51°, using the same thermometer. When dissolved in carbon bisulphide and treated with bromine water, it yields a *monobromo-derivative*, $C_4SBrMe_2{\cdot}COPh$, which melts at 85°; Keiser's compound melted at 77°. The formation of this compound disproves Marcusson's rule (Abstr., 1894, i, 16), that one is "unable to obtain thiophen derivatives having a halogen or nitro-group in the ortho-position relatively to a CO group." The monobromo-derivative yields a yellowish *oxime*, which melts at 176—177°, and does not, like the corresponding benzene derivatives, yield an indoxazen; probably the ortho-substituted oximes have a different stereometric configuration in the thiophen and benzene series.

2:3:5-*Dimethylthiophencarboxyl amide*, $C_4SHMe_2{\cdot}CONH_2$, was prepared by adding aluminium chloride to a solution of 2:5-dimethylthiophen and carbamide chloride in carbon bisulphide; it melts at 133—134°, and is hydrolysed by alcoholic potash to 2:3:5-*dimethylthiophencarboxylic acid*, $C_4SHMe_2{\cdot}COOH$, which melts at 117—118°. The corresponding derivatives of coal-tar thioxen melt at 119—120°, and 163—164° (Zelinski, 115—116° and 171—172°). The 2:3:5-acid yields a monobromo-derivative, $C_4SBrMe_2{\cdot}COOH$, melting at 188—189°; this affords another contradiction of Marcusson's rule.

C. F. B.

Addition of Sulphur to Unsaturated Organic Compounds. By ARTHUR MICHAEL (*Ber.*, 1895, **28**, 1633—1637).—Various unsatu-

rated organic compounds were caused to combine with sulphur by heating them with it in sealed tubes for 20 hours, at temperatures varying between 150—210°. Ethylic fumarate yields a compound, $S{:}C_2H_2(COOEt)_2$; this is a yellowish oil of unpleasant odour, and boils above 180° under 20 mm. pressure. Methylic and ethylic acetylenedicarboxylates unite with only half as much sulphur, yielding thiophen derivatives, $S\begin{matrix}C(COOMe){:}C\cdot COOMe\\ \vert\\ C(COOMe){:}C\cdot COOMe\end{matrix}$, &c.; the methylic compound forms colourless prisms, and melts at 126—128°; the ethylic compound is an oil, and boils, with slight decomposition, at 240—250° under 20 mm. pressure. Cinnamene also unites with sulphur, forming a compound C_8H_8S; this was obtained in an impure form as a reddish oil, boiling above 180° under 25 mm. pressure.

C. F. B.

An Acid, $C_5H_6O_2$, from Hexachloroketopentene. By Theodor Zincke (*Ber.*, 1895, **28**, 1644—1647).—The acid, $C_5H_6O_2$, obtained in small quantity, together with ethylidenepropionic acid (Abstr., 1893, i, 698; this vol., i, 131), when the acid, $C_4Cl_5\cdot COOH$, formed from hexachloroketopentene by the action of alkalis, is reduced with sodium amalgam, is now shown to be an unsaturated compound, probably containing two double linkings, for it unites with 2HBr, but only with 1 mol. of bromine, Br_2. *Butinenecarboxylic acid*, $C_4H_5\cdot COOH$, crystallises in large, colourless, lustrous, monoclinic plates, and melts at 102—103°; the *barium* and *calcium salts* were prepared, the latter crystallising with H_2O. With bromine, it yields *dibromopentenic acid*, $C_5H_6Br_2O_2$, which crystallises in colourless needles, and melts at 88—89°; with hydrobromic acid, it yields *dibromovaleric acid*, $C_5H_8Br_2O_2$, which crystallises in large, lustrous, colourless, apparently rhombic, prisms, melts at 51—52°, and is not identical with either of the three hitherto known dibromovaleric acids.

C. F. B.

Combination of Aluminium Chloride with Nitro-derivatives of the Benzene Series. By G. Perrier (*Compt. rend.*, 1895, **120**, 930—932).—The compound, $Al_2Cl_6,2PhNO_2$, described by Stockhausen and Gattermann (Abstr., 1893, i, 161), is readily obtained by the interaction of the calculated proportions of its proximate constituents in presence of carbon bisulphide, and forms large, crystalline lamellæ, melting at 85—87°. Other nitro-derivatives under like conditions yield strictly analogous compounds, as follows. *Paranitrotoluene*, large, yellow lamellæ, melting at 105°; *α-nitronaphthalene*, red needles, melting at 115° to a brown liquid, which decomposes suddenly at 130°; *metadinitrobenzene*, small, yellowish scales, melting at 65—67°; *dinitrotoluene*, a yellowish, oily liquid, which solidifies to an amorphous mass on cooling; *paranitranisoïl*, small, yellow crystals, melting at 120° to an orange liquid, with a violet fluorescence; *orthonitranisoïl*, a liquid, formed with difficulty, owing to the decomposition of a large proportion of the ether by the aluminium chloride.

According to Stockhausen and Gattermann (*loc. cit.*), acetic chloride combines with orthonitranisoïl and orthonitrophenetoïl in presence of aluminium chloride. Experiments with acetic and benzoic chlorides

and various nitro-derivatives of the hydrocarbons alone, or in the presence of carbon bisulphide, show, however, that this reaction is not applicable to nitro-derivatives of hydrocarbons. The acid chlorides have no action on the compounds of the nitrohydrocarbons with aluminium chlorides. If aluminium chloride is added gradually to a mixture of the nitro-hydrocarbon and the acid chloride, the compound of the nitrohydrocarbon with aluminium chloride is the sole product. If the nitrohydrocarbon is added to the double compound of aluminium chloride and the acid chloride, the latter is displaced, and the compound of the nitrohydrocarbon and aluminium chloride is formed.

C. H. B.

Action of Phosphorus Pentachloride on Aromatic Ethers. By WILHELM AUTENRIETH (*Arch. Pharm.*, 1895, **233**, 26—42).—The author has investigated the action of phosphorus pentachloride on mixed ethers of the benzene, naphthalene, and quinoxaline series, and finds that in all cases it reacts as a chlorinating agent, yielding a monochlorinated ether, together with phosphorus trichloride and hydrogen chloride. If the ether and pentachloride are mixed together and heated to 30°, a vigorous action takes place, the mass melts to a dark red liquid, hydrogen chloride is evolved, and phosphorus trichloride passes over between 70° and 90°. In no case, even with a large excess of the pentachloride and at a high temperature, was the formation of phosphorus oxychloride and the decomposition of the ether, as in the case of aliphatic ethers (Bachmann, Abstr., 1883, 726) observed.

Parachloranisoïl, obtained by the action of phosphorus pentachloride on anisoïl, is a colourless, aromatic oil, which boils at 195—196°, whereas Beilstein and Kurbatow (*Annalen*, **176**, 30) give 198—202° as the boiling point. On hydrolysis with concentrated hydrochloric acid at 200°, it yielded the parachlorophenol, which was characterised by the formation of its benzoyl derivative; the latter crystallises in pearly plates, which melt at 86°.

Parachlorophenetoïl is a thick, colourless oil, with an intense aromatic odour. It is slightly volatile with steam, and boils at 212—215°.

α-Chloro-β-naphthyl methyl ether, (Cl : OMe = 1 : 2) was prepared from β-naphthyl methyl ether and phosphorus pentachloride; it forms white, pearly plates, and melts at 78°. It is insoluble in water, but readily soluble in most organic solvents. The α-chloro-β-naphthol, obtained by the hydrolysis of the ether with concentrated hydrochloric acid at 200—250°, forms colourless, glistening plates and needles, which melt at 70°. It sublimes on further heating, and gives with alkalis violet fluorescent solutions. Its *benzoyl derivative* crystallises in plates, and melts at 101°.

Ethoxytrichloroquinoxaline is obtained by the action of phosphorus pentachloride (3 mols.) on the ethoxydihydroxyquinoxaline (1 mol.) of Autenreith and Hinsberg (Abstr., 1892, 734). It crystallises in small, yellowish, glistening needles, and melts at 144°. It is insoluble in water, but soluble in alcohol, ether, and chloroform. *Hydroxytrichloroquinoxaline* is obtained when this ether is hydrolysed with concentrated hydrochloric acid at about 200°. This hydroxytrichloroquinoxaline is practically insoluble in water, alcohol, ether, chloroform,

and acetic acid. It is, however, soluble in alkalis and in concentrated acids.

For the purposes of identification, the benzoyl derivatives of para- and orthochlorophenol were prepared and examined. The para-compound melts at 86° (see above), whereas the ortho-derivative is a highly refractive liquid, which boils at 314—316°.

When parachlorophenol is treated with benzene sulphochloride according to the Baumann-Schotten-Hinsberg method (Abstr., 1891, 49), the *parachlorophenylic benzenesulphonate*, $Cl{\cdot}C_6H_2{\cdot}O{\cdot}SO_2Ph$, is formed. This is a colourless, odourless oil, which is insoluble in water, but miscible with alcohol and with ether. J. J. S.

Tolyl Derivatives of Sulphur, Selenium, and Tellurium. By F. Zeiser (*Ber.*, 1895, **28**, 1670—1675).—Krafft and Lyons have already shown that the mercury in mercury diphenyl may be readily displaced by the elements of the sulphur group (Abstr., 1894, i, 448); in the present paper, the author shows that the mercury ditolyls behave in a similar manner towards those elements. *Diorthotolyl telluride*, $(C_6H_4Me)_2Te$, is prepared by heating mercury diorthotolyl with tellurium in a sealed tube at 225—235°; it crystallises from alcohol in small, rectangular plates, melts at 37—38°, and boils at 202·5° under 16 mm. pressure. It combines with bromine yielding the *tellurobromide*, $(C_6H_4Me)_2TeBr_2$, which forms pale yellow prisms with oblique terminal surfaces, and melts at 182°. The corresponding *diparatolyl telluride* forms small, lustrous, flat, white prisms, melts at 63—64°, and boils at 210° under 16 mm. pressure. The *tellurobromide* crystallises in thin, lustrous, yellow, rhombic tablets, melting at 201°.

Diorthotolyl selenide, $(C_6H_4Me)_2Se$, obtained by heating mercury diorthotolyl with selenium, crystallises from alcohol in small, rectangular plates, melting at 61—62°, and boiling at 186° under 16 mm. pressure. The *selenobromide* is obtained as a brownish-red precipitate of small needles; it is very unstable, decomposing at 84°. If the selenide is oxidised with nitric acid of sp. gr. 1·4, it yields a solution of the *nitrate* of diorthotolylselenyl oxide, which, on treatment with concentrated hydrochloric acid, gives a crystalline precipitate of *diorthotolyl selenochloride*, $(C_6H_4Me)_2SeCl_2$, the latter melts at 152—153° with decomposition, and on careful treatment with soda is converted into *diorthotolyl selenic oxide*, $(C_6H_4Me)_2SeO$, which forms glassy plates, and melts at 116°; it dissolves in hydrochloric acid, regenerating the chloride.

Diparatolyl selenide forms colourless, prismatic crystals, melting at 69—69·5°, and boiling at 196—196·5° under 16 mm. pressure, and the *selenobromide* crystallises in microscopic, yellow prisms with oblique terminal surfaces, and melts and decomposes at 162°. The *selenochloride* is a white precipitate, and melts at 177—178°, and the *selenic oxide* crystallises in small, white needles; it melts at about 90°, turns red litmus blue, and, like the ortho-compound, combines with acids.

Diorthotolyl sulphide is obtained by heating mercury diorthotolyl with sulphur, and crystallises in lustrous, colouress, rectangular plates, melting at 64°, and boiling at 175° under 16 mm. pressure.

H. G. C.

Nitroquinones. By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1386—1388).—The author, in conjunction with Zeitlin, has previously shown (Abstr., 1894, i, 184) that substituted diazobenzeneimides, when heated with sulphuric acid, lose nitrogen, and yield substituted amidophenols, probably with the formation of phenylhydroxylamine derivatives as intermediate products. When metanitrodiazobenzeneimide is treated with sulphuric acid, the nitroamidophenol,

$$[NH_2{:}NO_2{:}OH = 1 : 3 : 4],$$

is formed. When this is oxidised with potassium permanganate, the nitroquinone, $C_6H_3(NO_2)O_2$, is obtained. If the oxidation is carried out with small quantities of the phenol (0·5—1·0 gr.), the resulting quinone is quite pure. It is insoluble in cold water, and only slightly soluble in hot; dissolves sparingly in ether, benzene, and light petroleum, more readily in alcohol, acetic acid, acetone, and chloroform. The alcoholic solution, when rapidly cooled, yields golden-yellow crystals, which decompose at 206°. It is not volatile with steam, but dissolves in alkalis to a brownish-violet solution. When warmed with aniline and alcohol, it forms a *dianilidonitroquinone*, $C_{18}H_{13}N_3O_4$, which crystallises from alcohol or acetic acid in small needles of melting point 260°. In spite of many attempts, the author has not succeeded in preparing Étard's nitroquinone by the action of chromyl chloride on nitrobenzene. J. J. S.

Constitution of Phenoquinone. By C. LORING JACKSON and GEORGE OENSLAGER (*Ber.*, 1895, **28**, 1614—1617; compare Abstr., 1893, i, 563).—It is suggested that phenoquinone has a constitution similar to that of a hemiacetal, and the formula $C_6H_4(OH)_2(OPh)_2$ is proposed. It is shown that this formula is in harmony with the chemical behaviour of the substance. It would lead us to anticipate the existence of salts of phenoquinone, and these have been said not to exist. The authors have, however, prepared a blue *disodium salt* by treating phenoquinone with an alkaline solution of sodium β-naphthoxide, and also by the direct addition of sodium phenoxide to quinone in ethereal solution. C. F. B.

Guaiacol and its Derivatives. By FRITZ LÜDY (*Chem. Centr.*, 1895, i, 32; from *Schweiz. Woch. Pharm.*, 1895, **32**, 469—473).—A method for preparing pure crystalline guaiacol is given; it melts at 28·5°, boils at 203—204°, has a density of 1·1355—1·1370 at 18°, and is soluble in 50 parts of water. A modification of Reimer's method of synthesising oxyaldehydes is given, and serves in a patented process for preparing vanillin. W. J. P.

Nitrotoluquinol. By FRIEDRICH KEHRMANN and M. TIKHVINSKY (*Ber.*, 1895, **28**, 1542—1543).—Acetyldinitrotoluquinol (Abstr., 1889, 969) is accompanied by a small amount of *acetylnitrotoluquinol*. This crystallises in long, lustrous, lemon-yellow needles melting at 118—120°. *Nitrotoluquinol* crystallises in yellowish-red needles, and melts at 122—124°. It forms a deep bluish-violet coloured solution in alkalis. The *diacetyl-compound* crystallises in colourless tablets melting at 101—104°. A. H.

Action of Alcoholic Ammonium Sulphide on 1:2:4-Amidodinitrobenzene. By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 1707—1709).—Dinitraniline [$NH_2 = 1$; $(NO_2)_2 = 2:4$], when reduced with alcoholic ammonium sulphide, yields two nitrophenylenediamines, the orthodiamine is deposited first: the mother liquid is then evaporated to dryness, the residue extracted with dilute hydrochloric acid, and the remaining ortho-compound precipitated with dilute ammonia; if the filtrate is mixed with concentrated ammonia, and allowed to cool, the paradiamine is deposited. It is identical with Ladenburg's compound from nitrodiacetoparaphenylenediamine.

Dinitromethylaniline behaves like dinitraniline, and the amines are separated in a similar manner, the *para-compound*

$$[NHMe : NO_2 : NH_2 = 1:2:4]$$

crystallises from water in almost black plates with a bronze lustre; it melts at 109—110°, and is red when powdered. The *salts* crystallise readily, and their solutions, like that of the base, resemble magenta in colour.

1:2:4-Dinitrodiphenylamine, when reduced with ammonium sulphide, yields, in addition to the orthophenylenediamine, a second base which appears to be the para-compound. Heim's conclusion, that the reduction of aromatic dinitramines by means of ammonium sulphide gives orthodiamines only, is therefore incorrect.

J. B. T.

Nitro- and Amido-derivatives of Paraditolylamine. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 1647—1650).—In his work on the constitution of the safranines (this vol., i, 219), the author mentioned that a new safranine may be obtained by the action of quinone dichlorimide on metamidoditolylamine; in the present paper, he gives a detailed description of the mode of preparation and properties of the latter. In order to prepare it, paraditolylamine is nitrated in sulphuric acid solution at −10°, and the resulting crude metanitroditolylamine, which contains large quantities of unaltered ditolylamine, is reduced by zinc-dust in acetic acid solution; the product is then made alkaline, extracted with ether, and the evaporated extract distilled in a current of coal gas or carbonic anhydride. The distillate consists of a mixture of the amido-derivative and ditolylamine, which may be separated by fractional crystallisation from light petroleum. *Metamidoditolylamine*, $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4Me$, which crystallises in well-developed, colourless prisms, melting at 71° (corr.), may be readily diazotised.

If paraditolylamine is nitrated in acetic acid solution, it yields a *trinitroparadiphenylamine*, $C_{14}H_{12}N(NO_2)_3$, which crystallises from chloroform in prisms melting at 268°.

H. G. C.

Maximum Temperature of Formation and Temperature of Decomposition of some Aromatic Diazochlorides. By G. ODDO (*Gazzetta*, 1895, **25**, i, 327—339).—The substances obtained by the author during his attempts to prepare the fluoronitrobenzenes (Abstr., 1891, 553) are not amidoazo-compounds, as he supposed at the time, but diazoamido-derivatives; the compounds described as the meta-

and para-dinitramidoazobenzenes are the meta- and para-dinitrodiazoamidobenzenes described by Meldola and Streatfeild (Trans., 1887, 102, 434), and behave as such on heating with hydrochloric acid, fusion with β-naphthol, or treatment with ethylic iodide and alcohol. In order to explain the formation of these compounds, it must be admitted that in the process employed (*loc. cit.*) the diazofluoride is first formed and subsequently condenses with a second molecule of the base at a high temperature. The author has made a series of experiments, demonstrating that diazo-salts can be formed at 90—100°; thus, on passing nitrous anhydride into a hydrochloric acid solution of paranitraniline at 85—90°, paranitrodiazobenzene is formed, and is even produced at 100°, although the dry salt explodes at 85°. Further, dry metanitrodiazobenzene chloride explodes at 118°, and dry α-diazonaphthalene and orthodiazophenol chlorides decompose without explosion at 96° and 152° respectively, whilst the same salts can be prepared at 100°, 60°, and below 60° respectively by the ordinary method of diazotising by aid of amylic nitrite.

W. J. P.

Constitution of Diazo-compounds. By R. Walther (*J. pr. Chem.*, 1895, [2], **51**, 528—531 and 581—584).—It is generally acknowledged that the formula for diazobenzene which is at present accepted fails to explain all the reactions of the compound. Particularly is this the case with the reaction between diazobenzene chloride and bromaniline on the one hand, and that between diazobromobenzene chloride and aniline on the other hand; for these two reactions yield the same compound, whereas, according to Kekulé's formula for diazobenzene, they should yield isomerides. If nitrous acid be supposed to contain pentavalent nitrogen, the formation of an alkylic nitrite from an alcohol and nitrous acid could be expressed thus—

$$MeOH + HNO_2 = MeO{\cdot}NO(OH)H = MeO{\cdot}NO + H_2O.$$

So also the reaction between nitrous acid and aniline hydrochloride would be—

$$NH_3PhCl + HNO_2 = NH_2PhCl{\cdot}NO(OH)H = NHPhCl{:}NH{:}O + H_2O.$$

The latter formula would represent diazobenzene chloride in aqueous solution, and the constitution of free diazobenzene would be represented by PhN:NH:O. The compound produced by the interaction of diazobenzene and aniline would then have the formula

$$PhN{:}NH{:}NPh,$$

which would account for the identity of the products in the reactions referred to above.

Meldola and Streatfeild have shown that the reaction between metanitrodiazobenzene and paranitraniline, on the one hand, and that between paranitrodiazobenzene and metanitraniline on the other hand, yield one and the same compound. The constitution of this may be either $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$ or $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$.

If the first of these be correct, the decomposition of the compound with hydrochloric acid should yield metanitrochlorobenzene and paranitraniline, whilst the second formula should yield paranitrochlorobenzene and metanitraniline. As a fact, all four products are obtained when the compound is decomposed by hydrochloric acid.

If the constitution of diazobenzene derivatives be that suggested by the author, the above anomaly, and several similar ones which the author quotes in the paper, disappear. For in this case the product of the interactions just discussed would be represented by the formula $NO_2{}^{3}\cdot C_6H_4\cdot N{:}NH{:}N\cdot C_6H_4{}^{1}\cdot NO_2{}^{1}{}^{4}$, and a compound of this structure may be expected to be hydrolysed into $1:3\text{-}NO_2\cdot C_6H_4\cdot N{:}NH{:}O$ and $1:4\text{-}NH_2\cdot C_6H_4\cdot NO_2$, equally as well as into $1:4\text{-}NO_2\cdot C_6H_4\cdot N{:}NH{:}O$ and $1:3\text{-}NH_2\cdot C_6H_4\cdot NO_2$. The diazobenzene would immediately yield chloronitrobenzene with the hydrochloric acid, so that all four products named above may be expected. A. G. B.

Diazohaloïd Compounds. By Eugen Bamberger (*J. pr. Chem.*, 1895, [2], **51**, 585—591). This is a reply to Hantzsch (this vol., i, 349). Whilst it is true that a few diazohalogen compounds, particularly such as contain two or more halogen atoms, are unstable in the solid state but stable in solution, it is not permissible to generalise from these cases. Other points in Hantzsch's paper are criticised, and the author concludes that the feeble acid properties of diazobenzene are no argument against the ammonium formula $N{:}NPh\cdot OH$, since it is by no means uncommon for nitrogen which replaces three hydrogen atoms to impart acidity (compare $N{:}CH$ from CH_4; $N{:}C\cdot OH$ from $CH_3\cdot OH$). A. G. B.

Diazonium Compounds and Normal Diazo-compounds. By Arthur Hantzsch (*Ber.*, 1895, **28**, 1734—1753).—Since the discovery of the isodiazo-compounds, all the diazo-compounds previously known have been described as normal compounds, in contradistinction to the later known "iso"-compounds. Recently Bamberger has adopted Blomstrand's formula, $N{:}NR\cdot OH$, for the "normal" compounds, retaining the azo-formula, $RN{:}N\cdot OH$, for the iso-diazo-compounds. From the results of his investigations, the author has concluded that diazo-compounds of both types do in reality exist, but that some of the so-called normal diazo-derivatives are of one type and some of the other, and sums up his conclusions as follows. (1) The salts of diazobenzene with oxy-acids, and also the haloïd salts, contain the radicle $N{:}NPh$, which is strictly analogous to ammonium, behaving in all respects as a compound alkali-metal, and may therefore be termed "diazonium." The metallic salts, sulphonic acids, and cyanides have a composition analogous to that of the azo-compounds and oximes, containing the true diazo-radicle, $Ph\cdot N{:}N$, and these are capable of existing in two stereometric modifications, as already shown by the author. (2) Diazonium salts are converted very readily, especially in alkaline solution (that is, by means of hydroxyl ions), into normal syn-diazo-compounds, the reverse change being brought about by

acid. (3) The typical diazo-decomposition, $Ph{\cdot}N{:}N{\cdot}R = PhR + N_2$, only takes place directly with the syn-diazo-compounds, the other isomerides first undergoing an intramolecular change with formation of the isomeric syn-derivative. (4) Inner anhydrides of both diazonium compounds and of syn-diazo-compounds can exist, the former being analogous to betaïne, and the latter to azimidobenzene.

Benzenediazoniumsulphanic acid. $C_6H_4{\cdot}N{:}N$ (O bridging SO_2)

Betaïne. $CH_2<^{NMe_3}_{CO-}>O$

Syn-diazophenol. $C_6H_4<^{N}_{O}>N$

Azimidobenzene. $C_6H_4<^{-N}_{NH}>N$

(5) No diazo-haloïds of the formula RN:NCl are at present known, but coloured labile double compounds with cuprous haloïds have been prepared, which are totally different from the double salts of the diazonium compounds, the latter being colourless, stable, and very similar to the corresponding ammonium and potassium double salts.

In support of statement (1), the author adduces the neutrality of the solutions and the fact that the electrolytic dissociation of the solutions of these salts corresponds very closely with that of the analogous potassium and ammonium salts under similar conditions. (The detailed experiments on this point will be published later.) In further agreement with the alkaline character of the diazonium radicle is the formation of soluble salts even with the weakest acids; thus *diazonium carbonates* may be prepared by the action of freshly precipitated silver carbonate on solutions of the chloride, and the *nitrites* and *acetates* may be obtained in a similar manner. The solutions of benzenediazonium, and paranitrobenzenediazonium carbonate are unstable, but that of parabromobenzenediazonium carbonate is fairly stable at 0°; they have an alkaline reaction, and on boiling, decompose with evolution of nitrogen, but the tarry products contain scarcely any phenol. The solution of parabromobenzenediazonium nitrite is also the most stable, and on boiling yields nitrogen, but scarcely any phenol or bromonitrobenzene; none of the salts could be obtained in the solid form. The formation of stable double salts still further confirms the analogy of the diazonium and ammonium compounds; in addition to the already known platinochlorides, the author has prepared *cobaltinitrites*, which form yellow microcrystalline powders, but cannot readily be obtained pure. Of more importance are the double salts with mercuric chloride, obtained by the addition of mercuric chloride solution to aqueous diazonium haloïds; *benzenediazonium mercurochloride*, $PhN_2{\cdot}HgCl_3$, forms slender, white needles, decomposing at 122°, and closely resembles ammonium mercurochloride, NH_4HgCl_3, and, like the latter, crystallises either in the anhydrous form or with 1 mol. H_2O. *Parachlorobenzenediazonium mercurochloride*, $C_6H_4Cl{\cdot}N_2Cl,2HgCl_2 + 2H_2O$, is so stable that it may be recrystallised from boiling water, and then melts with decomposition at 139—140°; it corresponds with the potassium mercurochloride, $KCl,HgCl_2 + 2H_2O$. A double salt of diazonium chloride and

mercuric cyanide, $C_6H_5 \cdot N_2Cl, 2Hg(CN)_2 + H_2O$, can be prepared in a similar manner, and crystallises in needles which explode at 107°.

The proofs that the diazobenzene metallic salts, sulphonic acids, and cyanides have the azo-formula are mainly of an indirect nature, depending chiefly on the great differences observed between their properties and those of the diazonium compounds. If the potassium and silver salts had the constitution N:NPh·OK(or OAg), diazonium hydroxide must possess simultaneously basic and acid properties, a combination which has, however, never been observed in the case of the alkali-metals or compound radicles forming hydroxides analogous to those of the alkali-metals. In the case of the sulphonic acids, if these had the diazonium constitution it would form the first instance of the presence of the group $N \cdot SO_3M$ in a derivative of an ammonium base, and moreover, such compounds should, if the metal yields colourless salts, be also colourless, whereas the diazosulphonates are all coloured, like the azo-compounds. For the diazocyanides, in addition to the grounds already mentioned against the diazonium constitution, the author adduces the facts that although the diazonium haloïds are analogous in almost all respects to the corresponding alkali salts, the cyanides differ totally from the alkali cyanides, as they are coloured, are insoluble in water, do not conduct electricity, and appear to be incapable of forming double salts. The isomerism of these two salts cannot therefore be explained by supposing that the one is a diazonium and the other a diazo-derivative, but these facts are all in agreement with the supposition that they are stereometric isomerides, each being a true diazo-derivative. That the two diazosulphanilic acids are both true diazo-compounds has been shown by Gerilowski, whose results will shortly be published, and in this case also the only tenable hypothesis is that they are stereo-isomerides.

The second of the author's conclusions, namely, that the diazonium compounds are readily converted into syn-diazo-compounds, follows from the fact already mentioned, that benzenediazonium chloride is readily converted into the syn-diazobenzene potassium and the sulphonate and cyanide. A direct proof is also found in the fact that when the so-called diazosulphanilic acid (which, as will be shown in a later paper, is in reality the inner anhydride of benzenediazoniumsulphonic acid, and is a neutral substance) is treated with alkali (1 mol.), it is slowly converted into a syn-diazobenzenesulphonate, the solution again becoming neutral. Had the salt formed been a diazonium salt of the formula $\begin{matrix} C_6H_4 \\ | \\ SO_3 \end{matrix} > N:N$, it would certainly have had a strongly alkaline reaction. The conversion of diazonium into diazo-compounds is brought about most readily in alkaline solution, that is, under the influence of hydroxyl ions. The change from the diazonium to the diazo-constitution also explains the action of silver oxide on the diazonium haloïds, which is otherwise not readily understood. The action does not proceed according to the equation $PhN_2Cl + AgOH = AgCl + PhN_2 \cdot OH$, but requires double the amount of silver oxide, silver chloride and diazobenzene silver being formed, $PhN_2Cl + Ag_2O = PhN_2 \cdot OAg + AgCl$. The alkaline nature of moist silver

oxide is sufficient to bring about the conversion of the diazonium radicle into the diazo-radicle, and simultaneously with its formation the resulting diazo-hydroxide is converted into the silver compound. These experiments were repeated with numerous other diazonium haloïds, among which the bromides were found the most suitable; these may be readily prepared from the corresponding amido-compound by diazotising in alcoholic solution with hydrobromic acid and amylic nitrite, and precipitating with ether; *parabromobenzenediazonium bromide*, $BrC_6H_4N_2Br$, crystallises from hot alcohol in large yellowish plates, *paranitrobenzenediazonium bromide*, $NO_2C_6H_4N_2Br$, in lemon-yellow, very explosive plates, and *orthochlorobenzenediazonium bromide*, $ClC_6H_4{\cdot}N_2Br$, in straw-yellow needles, the aqueous solution of which hardly evolves any nitrogen on boiling.

When diazonium sulphates and carbonates are treated with baryta water, they also are not simply converted into barium sulphate or carbonate and the diazonium hydroxide, but yield in addition considerable quantities of syn-diazobenzene barium. The hydroxide formed consists chiefly if not exclusively of the syn-diazohydroxide.

The third conclusion, that only the syn-diazo-compounds undergo the typical diazo-reaction with evolution of nitrogen, is borne out by the behaviour of the syn-diazosulphonates and of syn-diazobenzene cyanide described in previous papers by the author. A new proof is found in the behaviour of free diazosulphanilic acid, which, as will be shown in a future paper by Gerilowski, is a diazonium compound, and is perfectly stable in solution at the ordinary temperature, whilst the corresponding syn-diazo-salt, which may be readily obtained from it, loses the whole of its nitrogen under similar circumstances. Further, if the diazonium compounds underwent direct decomposition into nitrogen and benzene in a manner analogous to the decomposition of ammonium chloride into ammonia and hydrochloric acid, the action should proceed more readily as the anion becomes less negative; but it is found that, on the contrary, the diazonium carbonate undergoes the typical decomposition much less readily than the chloride, and the latter yields phenol and not chlorobenzene. This is readily explained if we assume that water, like the alkalis, first converts the diazonium compound into syn-diazohydroxide and free acid; the former then decomposes into phenol and nitrogen, the action proceeding the more readily as the acid liberated is more active.

The reasons for the fourth conclusion will be considered in a later paper. The facts on which the fifth conclusion is based have already been partly given above, where it has been shown that colourless diazonium double salts with mercuric salts can be prepared. True diazo-haloïds have not yet been prepared, but the author has succeeded in obtaining double salts which differ totally from those of the diazonium derivatives. These are formed with cuprous chloride and bromide, the latter salts being the most stable. They are obtained by dissolving the cuprous salt in hydrochloric acid and adding a solution of the pure diazonium chloride. *Syn-diazobenzene cuprobromide*, $\begin{matrix}Ph{\cdot}N\\ \|\\ BrN\end{matrix}$, Cu_2Br_2, forms large, reddish-yellow needles, and decomposes on addition of water into cuprous bromide, nitrogen,

and bromobenzene, no diazonium bromide being re-formed. *Para-bromosyndiazobenzene cuprobromide*, $\begin{matrix}C_6H_4Br\cdot N\\ \|\\ BrN\end{matrix}Cu_2Br_2$, is similar to the foregoing, but is of a darker red. They differ from the diazonium salts, inasmuch as they are strongly coloured, although cuprous salts are themselves colourless, and also in their stability and in the manner in which they undergo decomposition. H. G. C.

Azo- and Azimido-Compounds. By WILLIAM G. MIXTER (*Amer. Chem. J.*, 1895, **17**, 449—453).—*Benzoylmetazoparatoluidide*, [Me : NHBz : N_2 = 1 : 4 : 5], is prepared by reducing benzoylmetanitroparatoluidide in alcohol with zinc and ammonia, and crystallising the precipitate from glacial acetic acid. It forms orange coloured crystals, melts at 242°, and is nearly insoluble in alcohol.

Acetylmetazo-orthotoluidide, [Me : NHAc : N_2 = 1 : 2 : 5], from acetylmetanitro-orthotoluidide (m. p. 202°; Beilstein and Kuhlberg, give 197°), crystallises in orange "fibres," does not melt at 310°, and is not very soluble in hot glacial acetic acid.

Benzoylazo-xylidide, [Me_2 : NHBz : N_2 = 1 : 3 : 4 : 5], from benzoylnitro-xylidide (m. p. 187°) separates from hot glacial acetic acid in orange "fibres," and decomposes without melting at 280—290°.

Benzoylazimidotoluene, [Me : N_2 : NBz = 1 : 4 : 5], is prepared by dissolving benzoyltoluylenediamine in hydrochloric acid, and passing nitrous fumes through the solution; the new compound is at once precipitated. It crystallises from alcohol in white "fibres," and melts at 125°.

Azimido-xylene was prepared by treating benzoylazimido-xylene (m. p. 111°) with hot concentrated hydrochloric acid and adding water; on cooling, benzoic acid crystallises and the azimido-xylene may be precipitated from the solution as a white powder by the addition of ammonia. It melts at about 186° and dissolves in hot water, alcohol, ether, nitric acid, and hydrochloric acid. A *silver* compound was prepared. A. G. B.

Action of Alcohols on Metadiazobenzenesulphonic Acid. By W. B. SHOBER and H. E. KIEFER (*Amer. Chem. J.*, 1895, **17**, 454—461).—In a series of experiments parallel with that conducted with paradiazobenzenesulphonic acid (Abstr., 1893, i, 639), the following conclusions have been arrived at:—(1) Methylic alcohol when heated with metadiazobenzenesulphonic acid under various pressures gives both benzenesulphonic acid and methoxybenzenesulphonic acid. At the highest pressures, the methoxy-compound is formed in greatest excess. (2) Ethylic alcohol gives similar results. (3) Propylic alcohol at ordinary pressures gives both reactions.

The metadiazo-compound is decomposed with much greater ease than is the para-compound, a few minutes generally sufficing in place of from two to eight hours. A. G. B.

Conversion of Hydrazines into Paradiamines. By JOHANNES THIELE and L. H. WHEELER (*Ber.*, 1895, **28**, 1538—1539).—Hydrazines, in which there is no substitution in the para-position, are

converted into paradiamines when heated with fuming hydrochloric acid (1—3 parts) at 200°; dilute sulphuric acid is not suitable, the yield being smaller, and part of the hydrazine being oxidised. Paraphenylenediamine and methylparaphenylenediamine were obtained in this manner from phenylhydrazine and unsymmetrical methylphenylhydrazine respectively. Paratolylhydrazine, and β-naphthylhydrazine gave paratoluidine, and β-naphthylamine respectively, together with ammonium chloride. Unsymmetrical diphenylhydrazine yielded only resinous products. J. B. T.

Action of Phenylhydrazine on Chloracetanilide. By HANS RUPE and GEORG HEBERLEIN (*Ber.*, 1895, **28**, 1717—1719).—The chief product of the interaction of phenylhydrazine and chloracetanilide is the unsymmetrical hydrazine derivative,

$$NH_2.NPh\cdot CH_2\cdot CO\cdot NHPh,$$

which crystallises in colourless needles and melts at 149°. A second compound, probably phenylhydrazineglyoxalic anilide, is formed simultaneously, it melts at 135°, and is more readily soluble in ether. Phenylhydrazidacetanilide readily reacts with ketones and aldehydes; the compounds with formaldehyde, benzaldehyde, and ethylic acetoacetate melting at 220°, 223°, and 158° respectively. The nitriso-derivative melts at 144° and is identical with the nitrosamine from anilidoacetanilide. When heated with sodium ethoxide, the hydrazidanilide yields a compound which is insoluble in acids and alkalis and melts at 273°; dilute alkalis or acids convert the hydrazidanilide into a substance which melts at 205°, and dissolves readily in alkalis. The aniline derivatives of chloracetic acid and those of ethylic chloracetate, yield compounds with phenylhydrazine which are quite different from one another. J. B. T.

Hydroxylamineisobutyric acid. By ALFRED WERNER and F. BIAL (*Ber.*, **28**, 1895, 1374—1379).—By the action of benzenylamidoxime (1 mol.) on ethylic α-bromisobutyrate (1 mol.) and potassium hydroxide (2 mols.) in alcoholic solution, the authors have obtained three different products, namely the potassium salt, esoanhydride and ethylic salt of benzenylamidoximeisobutyric acid. The alcohol was got rid of by evaporation and the potassium salt and the anhydride removed by extracting the residue with dilute soda. On treating the insoluble oily residue with dilute hydrochloric acid, a small quantity of dibenzenylazoxime, $CPh\langle\begin{smallmatrix}N\\N\cdot O\end{smallmatrix}\rangle CPh$, remained behind, but the amidoethereal salt dissolved in the form of its hydrochloride. This forms large crystals which melt at 154—155°. It is soluble in alcohol but insoluble in benzene and light petroleum. From this hydrochloride, *ethylic α-benzenylamidoximeisobutyrate*, $NH_2\cdot CPh{:}NO\cdot CMe_2\cdot COOEt$, was obtained on warming with potash; it melts at 37—38°, is readily soluble in ether and benzene, less soluble in alcohol and apparently insoluble in light petroleum.

Benzenylamidoximeisobutyric esoanhydride, $NH\langle\begin{smallmatrix}CO\cdot CMe_2\\CPh=N\end{smallmatrix}\rangle O$, is the main product formed, it can be isolated by acidifying the alka-

line solution above mentioned with dilute hydrochloric acid. It forms large plates, melts at 112°, and is insoluble in water and light petroleum, but dissolves in alcohol, ether, and benzene. It also dissolves readily in alkalis, and when heated with concentrated hydrochloric acid yields the *hydrochloride of the amido-acid*,

$$HCl,NH_2\cdot CPh{:}N\cdot O\cdot CMe_2\cdot COOH,$$

which crystallises from water in colourless prisms and melts at 182—185°. *Benzenylamidoximeisobutyric acid* is best obtained by the hydrolysis of the ethylic salt described above. It crystallises from alcohol in fan shaped needles which melt at 112°. The acid is readily soluble in alcohol and ether, sparingly in benzene, and insoluble in light petroleum.

α-Benzenylchloroximeisobutyric acid, $CPhCl{:}N\cdot O\cdot CMe_2\cdot COOH$, is obtained by the action of sodium nitrite solution at the ordinary temperature on a solution of the amido-acid in hydrochloric acid. It crystallises in plates, and is readily soluble in glacial acetic acid, alcohol, and ether, but only sparingly in hot water, and melts at 81°. The corresponding *bromo-acid* melts at 80°. If either the chloro- or bromo-acid is treated with sodium ethoxide *ethylbenzoximeisobutyric acid*, $OEt\cdot CPh{:}N\cdot O\cdot CMe_2\cdot COOH$, is formed; this is an oily substance which is insoluble in water, but dissolves readily in alcohol or ether. When heated with hydrochloric acid (50 per cent.), it is hydrolysed into ethylic benzoate and *α-hydroxylamineisobutyric acid hydrochloride*. The former may be removed by extraction with ether, and on evaporating the aqueous solution the hydrochloride separates in the form of prisms, which melt at 160—162°.

α-Hydroxylamineisobutyric acid, $NH_2\cdot O\cdot CMe_2\cdot COOH$, may be obtained by the action of freshly precipitated silver oxide (about 2 mols.) on the hydrochloride (1 mol.) and subsequent removal of the silver with hydrogen sulphide. The acid crystallises from water in crusts, melts at 137° and is readily soluble in water and in alcohol, but insoluble in ether, benzene, and light petroleum. The *nitrate* is readily soluble in water, and melts at 140°. The *sulphate* is more sparingly soluble in water than the nitrate, and melts at 185—188°. J. J. S.

Action of Benzimidomethyl Ether on Aromatic Ortho-compounds. By H. L. WHEELER (*Amer. Chem. J.*, 1895, **17**, 397—403).—*Benzimidomethyl ether*, was prepared by treating silver benzimide, suspended in dry ether, with excess of methylic iodide, adding more ether after the lapse of several days, filtering, and evaporating the ether (compare Tafel and Enoch, Abstr., 1890, 491). It is a pale yellow oil, still liquid at −30°, and soluble in acids, but precipitable from such solutions by alkalis. The *platinochloride* was prepared.

Benzimidomethyl ether undergoes condensation with orthamido-aromatic compounds when heated with them, methylic alcohol and ammonia being eliminated. In this way there have been prepared benzenylorthamidophenol (this Journal, 1877, i, 303), from the ether and orthamidophenol; benzenylorthamidothiophenol (benz-

amidophenyl mercaptan, Abstr., 1880, 386), from the ether and orthamidothiophenol; benzenylorthophenylenediamine (m. p. 280°; anhydrobenzoyldiamidobenzene, Abstr., 1881, 1131), from the ether and orthophenylenediamine; and benzenylorthotoluylenediamine (obtained by Hübner from benzometamidoparatoluidide and benzoic chloride, *loc. cit.*) from the ether and orthotoluylenediamine.

A. G. B.

Benzylenimide. By Edmund Thiele and Hugo Weil (*Ber.*, 1895, **28**, 1650—1655).—By the reduction of ortho- and para-nitrobenzyl chloride Lellmann and Stickel obtained two bases of the composition C_7H_7N, which they termed ortho- and para-benzylenimide, and they ascribed to the latter the constitution $C_6H_4<\overset{NH(1)}{\underset{CH_2(4)}{|}}$. The authors have been engaged in the examination of this substance, and in view of the paper by Dimroth and J. Thiele (this vol., i, 344), publish the results they have obtained up to the present.

The cryoscopic determination of the molecular weight in phenol solution has shown that the molecular formula of "parabenzylenimide" is four times as great as that given by Lellmann and Stickel, namely, $C_{28}H_{28}N_4$; it has not yet been obtained in a crystalline condition, but it has been found that under various conditions it takes up the elements of 1 mol. H_2O. Thus when boiled with formic acid, it yields a *formyl* derivative, $(C_7H_6N\cdot COH)_4,H_2O$, and with acetic acid the corresponding acetyl derivative $(C_7H_6NAc)_4,H_2O$. Hydrogen chloride in chloroform solution converts it into the compound

$$(C_{14}H_{14}N_2,HCl)_2,HCl,$$

which does not yield the free base on treatment with sodium carbonate solution, but a new substance $(C_7H_7N)_4,H_2O$. On treatment with nitrous acid, two of the nitrogen atoms are diazotised, and two combined with nitroso-groups; on boiling, the former are decomposed, and the elements of water simultaneously taken up, with formation of a compound probably of the composition

$$C_{28}H_{22}(NNO)_2(OH)_2,H_2O.$$

"Benzylenimide" combines with paranitrobenzaldehyde in chloroform solution, yielding in the cold an indistinctly crystalline, orange-yellow substance, which sinters at 175°, and has the composition

$$(C_{28}H_{22}N_4)(C_7H_5NO_2)_3,$$

showing that the action has proceeded in the normal manner, each amido-group having combined with 1 mol. of aldehyde, and the two imido-groups with a third. If the chloroform solution be boiled for a long time, this compound takes up the elements of water (obtained from the water formed in the first reaction) yielding the additive compound $C_{28}H_{22}N_4,3C_6H_7NO_2,H_2O$, which resembles the foregoing externally but melts at about 150°.

The so-called parabenzylenimide therefore contains two amido- and two imido-groups, and as it forms additive compounds so readily, probably contains an ethylene linkage. The basic groups are probably in the meta-position, as the substance does not combine with

phenanthraquinone or dihydroxytartaric acid. It yields no paratoluidine on reduction, but on distillation with zinc dust, yields aniline in quantity. H. G. C.

Derivatives of Metamethylbenzoylorthuramide. By STEFAN v. NIEMENTOWSKI (*J. pr. Chem.*, 1895, [2], **51**, 510—517; compare Abstr., 1889, 1065).—*Carboxethylorthamidoparatoluamide*,

$$[CONH_2 : Me : NH{\cdot}COOEt = 1 : 2 : 4],$$

is prepared by mixing orthamidoparatoluamide (m. p. 146°) with ethylic chloroformate, washing the mass with water after it has cooled, and recrystallising from alcohol. It forms long, white needles, melts at 171°, and dissolves in hot alcohol, ether, acetone, chloroform, and benzene, but only sparingly in hot water. When heated above its melting point, it evolves alcohol, and yields metamethylorthouramidobenzoyl, which melts at 317° (*cf. loc. cit.*).

Nitrometamethylbenzoylorthouramide, obtained by nitrating metamethylbenzoylorthouramide, crystallises from glacial acetic acid in quadrilateral tables (with 1 mol. acetic acid), or in small prisms. It blackens and melts at 326°, and is either insoluble, or only sparingly so, in most organic solvents; water does not dissolve it. The *ammonium* and *potassium* salts are freely soluble. The corresponding *amido*-compound crystallises in slender, grey needles, blackens and melts at 308°, and is practically insoluble in water and organic solvents; the *hydrochloride*, *nitrate*, and *sulphate* were prepared.

Dinitrometamethylbenzoylorthouramide is produced when metamethylbenzoylorthouramide is heated with nitric acid (1·53 sp. gr.) until oxides of nitrogen are no longer evolved, and the cooled liquid poured into ice-cold water. It separates from glacial acetic acid in six-sided crystals, which are active towards polarised light; it melts and decomposes at 294°, but in a capillary tube it melts at 280°; it dissolves in glacial acetic acid and amylic alcohol, but not in other solvents, The *ammonium*, *sodium*, and *barium* salts have been prepared.

The corresponding *diamido*-derivative forms lilac-grey needles, melts at 333°, and is very sparingly soluble in ethylic and amylic alcohols; dilute ammonia dissolves it, yielding a red solution with a greenish fluorescence. The *hydrochloride*, *nitrate*, and *sulphate* were prepared. The *acetyl* derivative does not melt below 345°.

A. G. B.

Derivatives of Anthranil. By PAUL FRIEDLAENDER and W. SCHREIBER (*Ber.*, 1895, **28**, 1382—1386).—Anthranil, C_7H_5NO, which Friedlaender and Henriques (Abstr., 1883, 187) regarded as the inner anhydride of anthranilic acid, is now shown to be, in all probability, the anhydride of phenylhydroxylamine aldehyde, and to have the constitution $C_6H_4<\begin{matrix}CH\\|\\N\end{matrix}>O$.

Dichloranthranil, ($Cl_2 : C : N = 1 : 4 : 2 : 3$). This was obtained by reducing dichlororthonitrobenzaldehyde (Gnehm, Abstr., 1884, 1028) with tin and acetic acid, and was purified by means of steam distillation. It is only very sparingly soluble in cold water, somewhat more so in hot, and readily in most organic solvents. It

forms small, yellowish needles, and melts at 96—97°. It dissolves in hot dilute mineral acids, and crystallises out unaltered, when the solution is allowed to cool. When warmed with dilute sodium hydroxide it dissolves, and is partially converted into dichloranthranilic acid which melts at 152°.

Metamethoxyanthranil.—Metamethoxybenzaldehyde was added to nitric acid (sp. gr. 1·46), which was cooled below 0°. The nitroaldehyde (m. p. 102°) was separated by means of fractional recrystallisation from benzene, and then reduced in the usual way. The resulting methoxyanthranil is an oil which slowly distils with steam, and has a pleasant aromatic odour. It forms a compound with mercuric chloride, which melts at 185°.

Methylenedioxyanthranil was obtained by the reduction of nitropiperonal (m. p. 95·5°). It distils but slowly with steam, and may be obtained from the distillate by the addition of common salt or mercuric chloride. It forms small, white needles, melts at 110·5°; and yields a compound with mercuric chloride; this is insoluble in cold, but readily soluble in hot water, and melts at 238°. When warmed with sodium hydroxide, methylenedioxyanthranil is partially converted into the corresponding *methylenedioxyanthranilic* acid which melts at 203°. J. J. S.

Glyoxylic acid. By Carl Boettinger (*Arch. Pharm.*, 1895, **233**, 100—104 and 111—118).—When glyoxylic acid (sp. gr. 1·32) is slowly added to a solution of paratoluidine in alcohol and ether a number of products are obtained, the chief of which are paratoluidine acetic acid, paratoluidine acetoparatoluidide, and paratoluylparamethylimesatin. The mixture is allowed to remain over night, the ether and part of the alcohol evaporated, the residue precipitated by the addition of water, and the precipitate thoroughly extracted first with ammonia and then with water. The toluidineacetic acid and tolulylmethylimesatin are thus dissolved, and may afterwards be separated by means of ether, whereas *paratoluidineacetoparatoluidide*,

$$C_7H_7\cdot N{:}CH\cdot CO\cdot C_7H_7,$$

is insoluble, and may be purified by washing with ether, extracting with benzene, and then dissolving in alcohol and precipitating with water. It forms a bright red powder, which is insoluble in cold ammonia and sodium hydroxide, and is decomposed when warmed with these reagents. It is readily soluble in alcohol and in benzene, and is decomposed into paratoluidine, paratoluidineurea, and a substance with an isonitrile smell.

Paratoluidineacetic acid, $C_7H_7\cdot N{:}CH\cdot COOH$, is insoluble in ether and benzene, sparingly soluble in water, but readily in all alkalis. It is also readily soluble in alcohol, and is precipitated on the addition of water in the form of a yellowish, crystalline powder which melts at 193°.

The *paratoluylparamethylimesatin* crystallises from alcohol in golden-yellow plates which melt at 259°. It is sparingly soluble in benzene, but dissolves in concentrated hydrochloric acid, and is thereby converted into paramethylisatin.

In continuation of his work on the condensation of aromatic hydrocarbons with ketonic and aldehydic acids (Abstr., 1881, 1035), the author shows that glyoxylic acid reacts with both benzene and toluene in the presence of concentrated sulphuric acid. The sulphuric acid is covered with a layer of the hydrocarbon, the whole cooled in snow, the glyoxylic acid is added slowly, and the mixture is then thoroughly shaken. Benzene and glyoxylic acid treated in this way yield a small quantity of diphenylacetic acid together with diphenylglycollide and dibenzilic acid. *Diphenylglycollide* is readily soluble in alcohol, chloroform, and ether, but insoluble in water, both hot and cold. It crystallises in small, colourless crystals, melts at 140°, and dissolves in warm concentrated sulphuric acid to a yellow solution. Toluene and glyoxylic acid yield *ditolylglycollide* and *ditolylic acid*. The former separates from ether in large, thin plates, melts at 131—132°, and is insoluble in water, but dissolves in ether, alcohol, and chloroform. The *ditolylic acid*, $C_{32}H_{30}O_5$, could not be obtained in a crystalline form; on the addition of a mineral acid to a solution of one of its salts, it separates out in white, flocculent masses. It is insoluble in water, but dissolves in ether, alcohol, and chloroform.

The author also describes a double salt of glyoxylic acid, which was obtained by treating a concentrated neutral solution of sodium glyoxylate with calcium chloride; it has the composition,

$$2NaC_2H_3O_4 + Ca(C_2H_3O_4)_2.$$

J. J. S.

Constitution of the Fluorindines. By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 1543—1546; compare this vol., i, 148).—The author adduces fresh synthetical evidence in favour of the formula proposed by Fischer and Hepp for the fluorindines, which has been criticised by Nietzki (this vol., i, 477). The products have all been analysed. *Chlorophenylfluorindine*, $C_6H_4<\overset{NH}{\underset{N}{>}}C_6HCl<\overset{N}{\underset{N}{>}}C_6H_4$, can readily be obtained pure by heating the condensation product of chlorodihydroxyquinone with phenylorthophenylenediamine (which has the formula $C_6H_4<\overset{N}{\underset{NPh}{>}}C_6H(ClO)\cdot OH$), with benzoic acid and orthophenylenediamine hydrochloride. The free *base* is a crystalline powder with a green, metallic lustre, whilst the *hydrochloride* forms lustrous plates, and is almost insoluble in alcohol.

Methylphenylfluorindine, $C_6H_4<\overset{NH}{\underset{N}{>}}C_6HMe<\overset{N}{\underset{NPh}{>}}C_6H_4$, is prepared in a similar manner from the hitherto undescribed condensation product of phenylorthophenylenediamine with dihydroxytoluquinone. The *hydrochloride* of the fluorindine is formed in almost quantitative amount, and crystallises in long needles with a bronze lustre. The alcoholic solution is deep blue, and is not fluorescent. The base is a lustrous, crystalline powder. This compound is the most readily soluble fluorindine which has hitherto been described. A. H.

Relations of the Safranines to the Mauveïnes and Indulines. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 1578—1585).—As pointed out by Nietzki (*Ber.*, **28**, 1354), the synthesis of a safranine by the oxidation of a mixture of a metamidodiphenylamine with a paraphenylenediamine may be, in certain cases, expressed by an asymmetrical formula. In some cases, however, this is not possible, and the symmetrical formula must therefore be preferred as being capable of adaptation to all the members of the group. Thus, methylmetatoluylenediamine readily yields a safranine,

$$NH{:}C_6H_3\!\leqslant\!\begin{matrix}N\\NMe\end{matrix}\!>\!C_6H_2Me{\cdot}NH_2,$$

when oxidised with paraphenylenediamine, the formula of which cannot be expressed by an asymmetrical formula.

The basicity of the safranines is shown by the solubility in acids of the diacetyl derivative, and is also rendered evident by the electrical conductivity of the solutions of the safranine salts, which behave in a similar manner to those of pararosaniline, methylene blue, and acridine yellow in this respect. It appears, further, that safranine, when pure, is free from water, the amount of water hitherto found in the substance being either water of crystallisation or adventitious moisture.

All these properties of the safranines point to the accuracy of the formula $HN{:}C_6H_3\!\leqslant\!\begin{matrix}N\\NR\end{matrix}\!>\!C_6H_3{\cdot}NH_2$, which was previously proposed for them by the author.

According to this formula, there should only be a monacetyl derivative of safranol, and this appears to be the case, whilst the coloured substance described by Nietzki and Otto (Abstr., 1888, 831) as diacetylsafranol must have some other constitution.

According to the formula proposed, the safranines and mauveïnes must belong to the same class of compounds, and it is probable that these substances are related to induline in the same manner as phenylene red is to eurhodine. A. H.

Relationship of Indulines to Safranines. By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 1709—1717).—The conversion of aposafranine into the simplest induline of the benzene series observed by O. Fischer and E. Hepp (*Annalen*, **286**, 187) is not in accord with the author's conception of the relationship of these compounds, he has therefore repeated their experiments, which he finds they have incorrectly interpreted; the results confirm his views. Fischer and Hepp state that when heated with aniline, aposafranine hydrochloride, $C_6H_3^4NH_2\!\leqslant\!\begin{matrix}^1N\\^2NClPh\end{matrix}\!>\!C_6H_4$, is converted into the hydrochloride of the simplest benzene induline, $^4NH{:}C_6H_3\!\leqslant\!\begin{matrix}^1N\\^2NPh\end{matrix}\!>\!C_6H_4$, and this, by treatment with alcoholic baryta water and a mixture of glacial acetic and hydrochloric acid, yields benzeneindone and its hydrate respectively,

$O{:}C_6H_3{<}\overset{1}{\underset{2}{N}}\!\!-\!\!\underset{NPh}{>}C_6H_4$ and $HO{\cdot}C_6H_3{<}\underset{NPh}{NOH}{>}C_6H_4$; they conclude that indulines and safranines are representatives of different classes of compounds which may be converted into one another by intramolecular rearrangement. The author has been led by his previous investigations to the conclusion that the unoxygenated induline bases and the indones are paraquinoïdal anhydrides of amido- and hydroxy-azonium bases respectively, and that their salts and hydrates are derived from the orthoquinoïdal azonium form. As the safranines are amido-azonium bases, the confirmation or otherwise of Fischer and Hepp's results must decide the question.

By the action of aniline on aposafranine hydrochloride, in the manner described by Fischer and Hepp, *aniline-aposafranine*, $HN{:}C_6H_2(NHPh){<}\overset{1}{\underset{2}{N}}\!\!-\!\!\underset{NPh}{>}C_6H_4$, and *hydro-aposafranine*,

$$H_2N{\cdot}C_6H_3{<}\underset{NPh}{NH}{>}C_6H_4,$$

are first formed, the latter is then oxidised by the air to aposafranine; the formation of water was clearly recognised. Aniline-aposafranine agrees in properties with Fischer and Hepp's "benzene-induline hydrochloride"; the specimen analysed by them was probably contaminated with dihydrochloride, which is decomposed by water, but is stable in presence of hydrochloric acid. The action of aniline on aposafranine and on quinones is therefore similar in principle. When heated at 160—170° with a mixture of glacial acetic acid and hydrochloric acid, aniline-aposafranine is resolved into aniline and hydroxybenzeneindone (Fischer and Hepp's benzeneinduline, see above), $O{:}C_6H_2(OH){<}\overset{1}{\underset{2}{N}}\!\!-\!\!\underset{NPh}{>}C_6H_4$, which is identical with the condensation product of | dihydroxyquinone and phenylorthophenylenediamine hydrochloride. The position of the aniline radicle in aniline-aposafranine is thus proved. The production of benzeneindone by the interaction of alcoholic baryta water and aniline-aposafranine is probably preceded by the formation of hydroxybenzeneindone, which is then reduced. The oxidation product of orthamidodiphenylamine is isomeric, not identical, with aniline-aposafranine, as it also yields hydroxybenzeneindone by the action of hydrochloric acid, its formula must be $NPh{:}(NH_2)C_6H_2{<}\overset{1}{\underset{2}{N}}\!\!-\!\!\underset{NPh}{>}C_6H_4$; both the base and its salts closely resemble those of aniline-aposafranine, but it is more feebly basic, and, in ethereal solution, absorbs carbonic anhydride only slowly. It melts at 189—190°; Fischer and Hepp state that it does not melt even at 240°. The hydrochlorides of the two bases differ in crystalline habit, that of aniline-aposafranine being the less soluble. Aposafranine hydrochloride, when heated with dilute soda, readily yields benzeneindone, the compounds therefore bear the same relationship as rosinduline and rosindone.

With aposafranine hydrochloride, paratoluidine reacts like aniline, and forms *paratoluidine-aposafranine*, which crystallises in reddish-brown prisms with a blue sheen; it melts at 219—220°, and dissolves in sulphuric acid with a reddish-violet colour, which does not change on dilution. Solutions of the base are yellowish-red. The *hydrochloride* is deposited in bronze, lustrous prisms; it is more soluble than the corresponding aniline compound, and in this it differs from the base, which is less soluble. When heated with hydrochloric acid and glacial acetic acid at 160—170°, hydroxybenzeneindone, paratoluidine, and ammonia are formed. J. B. T.

Isomeric Forms of Diacetylthymoquinonoxime. By E. Böhm (*Ber.*, 1895, **28**, 1547—1549).—*Diacetylthymoquinonoxime* crystallises from light petroleum in two forms, compact needles, and very thin plates with a nacreous lustre. Both of these melt at 110°, but the formation of the plates seems to be favoured by previously heating the solution for some time. The plates are obtained free from needles when iodine is added to the solution in petroleum. The *monacetyl compound* is formed when the diacetyl derivative is heated above its melting point or is treated with iodine in alcoholic solution. A. H.

Iodonium Bases from 1 : 2-Iodotoluene. By M. Heilbronner (*Ber.*, 1895, **28**, 1814—1816).—These and their salts were prepared as described by V. Meyer and Hartmann (Abstr., 1894, i, 242, 461); the corresponding derivatives from 1 : 4-iodotoluene and from 1 : 4-chloriodobenzene have been already prepared respectively by McCrae and by Wilkinson (this vol., i, 221). The salts described are insoluble, or very sparingly soluble in water; the temperatures given are melting points.

The *base*, $OH{\cdot}I(C_6H_4Me){\cdot}C_6H_3MeI$, is only known in aqueous solution. The *iodide* is a yellow powder; the *bromide* a white powder, 162°; the *chloride* a white powder, 162·5°; the *dichromate* a yellow powder, 152°; the *mercurochloride* a white powder, 137°.

The *base*, $OH{\cdot}I(C_6H_4Me)_2$, is also only known in aqueous solution. The *iodide*, 152°, forms white needles, turning yellow when exposed to light, and yields 1 : 2-iodotoluene when distilled; the *periodide*, 155°, is decomposed by water and by alcohol. *Bromide*, white needles, 178°. *Chloride*, white needles, 179°. *Dichromate*, yellow needles. *Mercurochloride*, white plates, 133—134°. *Platinochloride*, flesh-coloured precipitate, or tiny, yellow iridescent needles, 169°. *Aurochloride*, yellow needles, 108°. C. F. B.

Dichlorobenzylideneacetone. By Carl Goldschmidt (*Ber.*, 1895, **28**, 1532).—*Dichlorobenzylideneacetone*, $CHClPh{\cdot}CHCl{\cdot}COMe$, is prepared by the action of chlorine on benzylideneacetone in chloroform solution; it crystallises in colourless needles and melts at 93°. When treated in alkaline solution with hydroxylamine hydrochloride, *chlorobenzylideneacetoxime*, $CClPh{:}CH{\cdot}CMe{:}NOH$, is formed which melts at 133°, and by the action of soda yields a *methylphenylisoxazole*, $CPh\begin{matrix}CH{\cdot}CMe\\ \|\quad\|\\ O\text{—}N\end{matrix}$; this has a neutral reaction, readily dissolves in strong acids, is reprecipitated on dilution, and is volatile with steam.

Attempts to prepare chlorisoquinoline by the action of dehydrating agents on chlorobenzylideneacetoxime were unsuccessful, but when treated with phosphoric anhydride or fuming sulphuric acid, chlorocinnamaldoxime yields a *chlorisoquinoline* which crystallises and melts at 45°. The picrate melts at 177°. The yield was small.

J. B. T.

Ionone and Irone. By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1895, **28**, 1754—1758; compare Abstr., 1894, i, 80).—Ionone readily combines with semicarbazide in acetic acid solution forming *iononesemicarbazone*, $C_{13}H_{20}:N\cdot NH\cdot CO\cdot NH_2$, which crystallises from its benzene solution, on the addition of light petroleum, in thin needles melting at 109—110°; it is gradually resolved by mineral acids into ionone and semicarbazone. The isomeric irone also forms a semicarbazone, but this has only been obtained as an oil, which is much more soluble in a mixture of light petroleum and benzene than the foregoing compound.

Iononeparabromophenylhydrazone, $C_{13}H_{20}:N\cdot NH\cdot C_6H_4Br$, is obtained by the action of parabromophenylhydrazine on ionone in cold acetic acid solution. It is best recrystallised from slightly diluted methylic alcohol, when it forms long characteristic plates which sinter at 134° and melt at 140—145°; it is resolved by hydrochloric acid into ionone and parabromophenylhydrazine, the former being recognised by its characteristic odour of violets. When the hydrazone is boiled with acetic acid, it undergoes intramolecular change forming a compound termed by the authors *isoiononeparabromophenylhydrazone*; this crystallises in pale yellow prisms, melts at 165°, and is no longer hydrolysed by acids. *Ironeparabromophenylhydrazone*, $C_{13}H_{20}:N\cdot NH\cdot C_6H_4Br$, is prepared in a similar manner to the ionone derivative, and forms concentric aggregates of needles which soften at 156° and melt at 168—170°. When a mixture of ionone and ironeparabromophenylhydrazone is dissolved in warm acetic acid and precipitated by the gradual addition of water, the irone derivative is first deposited, and the two compounds may be separated in this manner.

The conversion of both ionone and irone into hydrazone is complete if an excess of the hydrazine is employed, and the reaction may therefore be employed for the quantitative estimation of these substances.

H. G. C.

Coloured Alkaline Solutions of 1 : 3 : 5-Dinitrobenzoic acid.—By A. SHUKOFF (*Ber.*, 1895, **28**, 1800—1803).—V. Meyer (this vol., i, 91) has described the variously coloured solutions obtained on dissolving 1 : 3 : 5-dinitrobenzoic acid in an alkali. The first four solutions must contain the original acid, for this is obtained from them when they are acidified; the difference in colour which they exhibit must be due to their containing different salts, normal and basic, of the acid; in some of these, hydrogen atoms of the benzene ring have been replaced by metal. The last, magenta-coloured solution contains two new acids, one of which is precipitated when the solution is acidified, whilst the other remains in solution. The first is a white or brownish powder which decomposes and melts above 200°; it appears to be *dinitroazoxybenzoic acid*,

$$O<\begin{matrix}N\cdot C_6H_3(NO_2)\cdot COOH\\ |\\ N\cdot C_6H_3(NO_2)\cdot COOH\end{matrix}.$$

The second, which is formed in much smaller quantity, is a yellow, amorphous powder; it melts and decomposes below 200°, and its solution in caustic alkalis is magenta coloured; it appears to be an *azoxytrihydroxybenzoic acid*, $O<\begin{matrix}N\cdot C_6H(OH)_3\cdot COOH\\ |\\ N\cdot C_6H(OH)_3\cdot COOH\end{matrix}$.

C. F. B.

Diamidobenzoic acids. By Carl Haeussermann and H. Teichmann (*J. pr. Chem.*, 1895, [2], **51**, 526—528).—Ethylic 3 : 5-diamidobenzoate is best prepared as follows:—A hot solution of ethylic 3 : 5-dinitrobenzoate (9 parts) in alcohol (90 parts) is gradually added to a mixture of tin (15 parts) and hydrochloric acid of sp. gr. 1·19 (30 parts), and the whole is heated on the water bath until the tin has dissolved. Ten times the volume of water is now added, the alcohol is evaporated, and the solution made alkaline with ammonia and shaken with ether. The ethereal solution is dried with caustic soda, the ether distilled, and the residue dissolved in five times its weight of absolute alcohol; to this solution sulphuric acid (1 : 1) is added, and the precipitated sulphate is re-crystallised, dissolved, decomposed with ammonia, and the liberated ethereal salt extracted with ether.

Ethylic 3 : 5-diamidobenzoate melts at 84°; with hydrochloric acid and a nitrite, it gives the yellow colour characteristic of diamines; when heated with quicklime, it yields calcium carbonate, phenylenediamine, and ethylene. The *hydrochloride*, $C_6H_3(NH_2)_2\cdot COOEt,2HCl$, *sulphate*, with $2H_2O$, *picrate* and *diacetyl* derivative (m. p. 184°) are described.

A. G. B.

Phenylnitrocinnamic acids and their Stereoisomerides. By Marussia Bakunin (*Gazzetta*, 1895, **25**, i, 137—189).—Ortho-, meta-, or para-phenylnitrocinnamic acid may be prepared by heating the corresponding nitrobenzaldehyde with sodium α-toluate and acetic anhydride in a reflux apparatus for six hours; the solid product of the reaction is extracted with hot water, precipitated with cold water, and the precipitated acid purified by dissolving it in soda and precipitating with hydrochloric acid.

Phenylorthonitrocinnamic acid, $NO_2\cdot C_6H_4\cdot CH{:}CPh\cdot COOH$, purified by aid of its barium salt, crystallises from alcohol in yellow, anorthic prisms melting at 195—196°; its *sodium* salt crystallises in beautiful yellow, anorthic tablets containing $5H_2O$ which is lost at 80—90°. The *barium* salt crystallises with varying quantities (5 to $11H_2O$) of water in efflorescent needles, whilst the sparingly soluble *silver* salt is obtained as a yellowish precipitate. The *methylic* salt crystallises in yellow orthorhombic prisms melting at 75—76°, and has the normal molecular weight in freezing acetic acid.

On evaporating the ethereal extract of the mother liquor obtained in the preparation of the foregoing acid, an *acid* isomeric with it separates; it forms short, monosymmetric, yellow crystals melting at 146—147°. Its *silver* salt is yellow, and differs in appearance from that obtained from the acid melting at 195—196°; the *methylic* salt

crystallises in long, yellow needles melting at 94—95°, and was found to have the normal molecular weight by cryoscopic determinations in acetic acid. The relation between the two acids seems to be the same as that between cinnamic and allocinnamic acids, with the difference, however, that no interconversion of the acids or their methylic salts could be effected.

On attempting to prepare phenylmetanitrocinnamic acid by the above process, a crude mixture of two *isomerides* was obtained which was only purified and separated with difficulty by fractional crystallisation of the very soluble magnesium salts, and fractional crystallisation from alcohol of the acid liberated from the various fractions. One of the acids thus obtained crystallises in yellowish, lustrous prisms melting at 181—182°, and is rather less soluble in alcohol than its isomeride, which crystallises in thin needles melting at 195—196°. The *sodium* salt of the former crystallises in yellowish needles containing $6H_2O$, and the *barium* salt forms lustrous, yellow needles containing $2H_2O$; the *silver* salt is a white powder; the *methylic* salt obtained from it crystallises in long, yellow, monosymmetric prisms melting at 78—79°. The *sodium* salt of the acid melting at 195—196° crystallises in hard, yellow needles; the *barium* salt forms yellow, anorthic prisms containing at least $4\frac{1}{2}H_2O$, and the *methylic* salt, prepared from the silver salt, crystallises in yellow, mica-like plates melting at 114—115°.

Two stereoisomeric *phenylparanitrocinnamic acids* can be prepared in a similar manner to the above; one of these crystallises in yellow prisms or needles, and yields a *sodium* salt which forms long, yellow needles containing $4H_2O$, a *barium* salt which crystallises in yellow, monosymmetric tablets containing $1H_2O$, a *silver* salt which forms lustrous, pearly laminæ containing $1H_2O$, and a *methylic* salt which crystallises in yellow, monosymmetric needles melting at 141—142°. The isomeric acid crystallises in orthorhombic, pleochroic, yellow needles melting at 95—105° and containing $1H_2O$ which is readily lost giving the anhydrous acid which melts at 140—142°; it crystallises from alcohol with $\frac{1}{2}$EtOH, and from benzene in beautiful, efflorescent laminæ containing about $\frac{1}{4}C_6H_6$ which melt at about 120° with evolution of benzene. The *sodium* salt crystallises in thin, yellow needles containing at least $3\frac{1}{2}H_2O$; the *barium* salt forms needles containing $2H_2O$; the *silver* salt is a yellow powder, and the *methylic* salt melts at 147—148·5°.

On reducing phenylorthonitrocinnamic acid in dilute alcohol with sodium amalgam, *phenylhydrocarbostyril*, $\begin{matrix}CHPh\cdot CO\\ |\\ CH_2—C_6H_4\end{matrix}>NH$, is obtained in yellow needles melting at 173—174°; it is accompanied by *phenylorthoamidocinnamic acid*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot COOH$, a yellow powder melting at 147—149°, and insoluble in the ordinary solvents.

No well-crystallised substance could be isolated from the reduction product of phenylmetanitrocinnamic acid.

Phenylparanitrocinnamic acid, on reduction with sodium amalgam, yields *phenylparamidocinnamic acid* in microscopic, yellow prisms melting at 200—201°; its *hydrochloride*, $C_{15}H_{15}NO_2,HCl$, crystallises

in needles melting at 148—149°, and the *sulphate*, $(C_{15}H_{15}NO_2)_2,H_2SO_4$, is also crystalline, and melts at 220° with decomposition. The amido-acid is converted into *phenylhydroparacoumaric acid*, $OH\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot COOH$, by the action of nitrous fumes; it crystallises in white laminæ melting at 179—180°, and may also be prepared by reducing phenylparacoumaric acid with sodium amalgam.

W. J. P.

Crystallography of the Phenylnitrocinnamic acids and their Derivatives. By Eugenio Scacchi (*Gazzetta*, 1895, **25**, i, 310—326).—The author has made a crystallographic examination of many of the compounds recently described in the preceding abstract. No results of theoretical importance have been obtained. W. J. P.

Constitution of Coumarone. By Gustav Komppa (*Ber.*, 1895, **28**, 1643—1644).—The author has already shown (Abstr., 1894, i, 130) that coumarone contains a ring of five members, and has the formula $C_6H_4<\overset{CH}{\underset{O}{>}}CH$. Dennstedt and Ahrens (this vol., i, 475) seem to have overlooked this. C. F. B.

Intramolecular Rearrangement of Unsaturated Acids. So-called Phenylhydroxycrotonic acid. By Rudolph Fittig (*Ber.*, 1895, **28**, 1724—1725).—"Phenylhydroxycrotonic acid" is identical with benzoylpropionic acid, as proved by comparison of the salts and of the free acids. Since E. Fischer and Stewart (Abstr., 1892, 1447) have shown that phenylhydroxycrotononitrile has the formula $CHPh{:}CH\cdot CH(OH)\cdot CN$, the treatment with hydrochloric acid must cause an intramolecular rearrangement from

$$CHPh{:}CH\cdot CH(OH)\cdot COOH$$

to $COPh\cdot CH_2\cdot CH_2\cdot COOH$; of this no explanation can at present be given. Tiemann and Biedermann's statement (Abstr., 1893, i, 471) that, when reduced with sodium amalgam, "phenylhydroxycrotonic acid" yields phenylhydroxybutyrolactone is incorrect; like benzoylpropionic acid, it gives phenylbutyrolactone. J. B. T.

Quinone-bis-amidobenzoic acid. By Jules Ville and Charles Astre (*Compt. rend.*, 1895, **120**, 878—880).—The acid (this vol., i, 465) dissolves readily in dilute aqueous potash, yielding a red-brown solution, which alters when exposed to air, and from which carbonic anhydride precipitates the greater part of the acid. The potassium salt, $C_6H_2O_2(NH\cdot C_6H_4\cdot COOK)_2 + 2H_2O$, is precipitated in slender needles on adding a mixture of alcohol and ether to the solution; it becomes anhydrous at 100—105°. Its solutions have no reducing action on silver nitrate or Fehling's solution.

The dibenzoyl derivative, $C_6HCl(OBz)_2(NH\cdot C_6H_4\cdot COOH)_2$, is an ochre-yellow substance, insoluble in water and light petroleum, and slightly soluble in other ordinary organic solvents. When heated with dilute sulphuric acid, it yields benzoic acid.

The nitroso-derivative, $C_6H_2O_2[N(NO)\cdot C_6H_4\cdot COOH]_2 + H_2O$, is obtained by the action of sodium nitrite on the acid previously dis-

solved in a mixture of glacial acetic acid (2 parts) and nitric acid (1 part). It is a deep red substance, which loses its water at 105°, intumesces at 180°, and decomposes when more strongly heated. It is insoluble in light petroleum, almost insoluble in water and benzene, somewhat soluble in alcohol, ether, and chloroform.

Reducing agents seem to convert quinone-bis-amidobenzoic acid into a corresponding quinol derivative, which is very unstable, and has not yet been isolated. It reduces Fehling's solution and ammoniacal silver nitrate.

It would seem that the quinonic function persists in quinone-bis-amidobenzoic acid, and since Knapp has shown that the products of the action of chloroquinones on primary amines are also quinonic, it follows that the constitution of the quinone-bis-amidobenzoic acid is that ascribed to it already. C. H. B.

Indole from Orthodiamidostilbene. By JOHANNES THIELE and OTTO DIMROTH (*Ber.*, 1895, **28**, 1411—1414).—The authors have prepared the two stereoisomeric orthodinitrostilbenes from orthobenzylic chloride and alcoholic potash by Bischoff's method. They find that the two are best separated by recrystallisation from epichlorhydrin and then from ethylic acetate. The *trans*-compound, which is less soluble in epichlorhydrin than the *cis*-, melts at 191—192° (Bischoff gives 196°). The *cis*-derivative, after recrystallisation from ethylic acetate, melts at 126°. In order to prepare the *trans*-diamidostilbene, the authors recommend the use of stannous chloride and acetic acid saturated with hydrogen chloride as the reducing agents. The *trans*-diamidostilbene, after recrystallisation from benzene, melts at 168° (Bischoff, 176°). The *hydrochloride* is sparingly soluble in water, and crystallises with $2H_2O$, which it loses at 100°.

The *cis-diamidostilbene* was prepared in a similar manner from the *cis*-dinitro-compound. It forms small red needles, and melts at 123°. The *hydrochloride*, which was obtained as a greyish powder by precipitating the ethereal solution of the base with hydrogen chloride, melts at 230°.

In order to obtain a good yield of indole, a mixture in molecular proportions of the *trans*-diamidostilbene and its dihydrochloride is distilled for about three-quarters of an hour at 170—185° in a vacuum. The monohydrochloride is the first product formed, and this is then decomposed into indole and aniline hydrochloride. This latter then reacts with a further quantity of the diamidostilbene hydrochloride, forming aniline and the dihydrochloride of the diamidostilbene. Thus at the end of the reaction all the free base which was present at the beginning has passed over in the form of indole and aniline, whereas the dihydrochloride remains behind in the retort in a pure state. The distillate is then acidified, saturated with common salt, and subjected to steam distillation, whereby the indole passes over in almost theoretical quantity.

Cis-diamidostilbene also yields indole when heated, but as it is more difficult to obtain in large quantities, it is not so useful a source for indole as the *trans*-compound. J. J. S.

Constitution of Indene. By WILLY MARCKWALD (*Ber.*, 1895, **28**, 1501—1505).—With benzaldehyde, indene readily forms a condensation product which separates from alcohol in yellow crystals, and melts at 135°. This substance is *hydroxybenzylindene*,

$$CH\lessgtr\begin{matrix}C_6H_4\\CH\end{matrix}\!\!>CH\cdot CHPh\cdot OH.$$

The *acetate* crystallises in orange-yellow prisms, melting at 110—111°. When indene is treated with amylic nitrite and sodium ethoxide, an isonitroso-compound is formed as a reddish-yellow oil, which is readily soluble in alkalis, but has not yet been obtained pure.

Methylindene reacts in a similar manner both with benzaldehyde and amylic nitrite, but the products of the action have not been obtained pure. Neither hydrindene nor coumarone undergo either of these changes.

This remarkable behaviour of the methylene group of indene is probably due to the acidifying effect of its position in a ring of five atoms, and is a further argument in favour of the analogy of indene and methylindene to indole, and against the formula for indene proposed by Dennstedt and Ahrens (this vol., i, 475). A. H.

β-Metatolyl-αγ-diketohydrindene. By EDUARD BRAUN (*Ber.*, 1895, **28**, 1388—1393).—When xylylidenephthalide (Heilmann, Abstr., 1890, 625) is suspended in alcohol and heated during an hour with sodium methoxide, it is converted into the *sodium derivative of tolyldiketohydrindene* (compare Abstr., 1893, i, 415), which crystallises from water in red needles. When an aqueous solution of the sodium derivative is warmed with acids, the red colour disappears, and the *metatolyldiketohydrindene* itself, $C_6H_4{:}(CO)_2{:}CH\cdot C_7H_7$, separates; this crystallises in white plates, and melts at 134—135°. It is insoluble in water, but readily soluble in most other solvents. It dissolves in alkalis, yielding a yellow solution, from which it is precipitated unaltered on the addition of acids. The *phenylhydrazone* crystallises in long, yellow needles, melts at 167—168°, is soluble in benzene and toluene, and dissolves in concentrated sulphuric acid yielding a dirty green solution. The *dioxime* is obtained on warming the diketone with hydroxylamine hydrochloride and sodium hydroxide in dilute alcoholic solution until the colour changes from red to yellow; it forms colourless crystals, which decompose at 222°, and is sparingly soluble in benzene, but readily in methylic and ethylic alcohols.

Tolylbromodiketohydrindene, $C_6H_4{:}(CO)_2{:}CBr\cdot C_7H_7$, is obtained by brominating the diketone; it crystallises in colourless plates, melts at 88°, and does not show the acid reactions of the diketone. The corresponding *chloro-derivative*, $C_6H_4{:}(CO)_2{:}CCl\cdot C_7H_7$, crystallises from alcohol in colourless plates, which melt at 92—93°.

Tolyldiketohydrindeneanilide, $C_6H_4{:}(CO)_2{:}C(NHPh)\cdot C_7H_7$, obtained by warming the bromo- or chloro-derivative with aniline, crystallises in yellow needles, and melts at 171°.

Tolylbenzoyldiketohydrindene, $C_6H_4{:}(CO)_2{:}CBz\cdot C_7H_7$, is obtained when the diketone is heated with an excess of benzoic chloride and

then boiled with dilute sodium hydroxide. It crystallises in yellowish-red needles, and melts at 112—113°.

Phenylbenzoyldiketohydrindene, $C_6H_4{:}(CO)_2{:}CBz{\cdot}Ph$, was prepared by treating phenyldiketohydrindene (Abstr., 1894, i, 37) with benzoic chloride. It crystallises from benzene in small, yellow prisms, and melts at 168°. Tri-oximes corresponding with the last two compounds could not be obtained.

Methyltolyldiketohydrindene, $C_6H_4{:}(CO)_2{:}CMe{\cdot}C_7H_7$, is formed when a solution of the sodium salt of the diketone in methylic alcohol is heated with excess of methylic iodide. It crystallises in colourless plates, and melts at 97°.

The *ethyltolyldiketohydrindene* melts at 63—65°, and is readily soluble in most solvents except light petroleum.

Ethylic tolyldiketohydrindene acetate,

$$C_6H_4{:}(CO)_2{:}C(C_7H_7){\cdot}CH_2{\cdot}COOEt,$$

obtained by the action of ethylic monochloracetate on the sodium derivative of the diketone at 100°, crystallises from methylic alcohol in colourless, quadratic plates, and melts at 116—118°.

Bistolyldiketohydrindene,

$$C_6H_4{:}(CO)_2{:}C(C_7H_7){\cdot}C(C_7H_7){:}(CO)_2{:}C_6H_4,$$

is obtained when the diketone is oxidised with nitrous acid. It crystallises in small, white needles, and melts at 203—205°.

Benzylphenyldiketohydrindene, $C_6H_4{:}(CO)_2{:}CPh{\cdot}CH_2Ph$, obtained by the action of benzylic chloride on the sodium derivative of phenyldiketohydrindene, forms colourless crystals, and melts at 105—106°.

Cyanometaxylylidenephthalide, $CO{<}\overset{C_6H_4}{\underset{O}{\quad}}{>}C{:}C(CN){\cdot}C_7H_7$, is formed when equal quantities of metatolylacetonitrile and phthalic anhydride are heated with a small quantity of sodium acetate; it forms lemon-yellow needles, which melt at 144—145°. When treated with sodium ethoxide, it is not converted into a diketo-compound. It yields a *dinitro-derivative*, $C_{17}H_9N(NO_2)_2O_2$, when added to fuming nitric acid; this separates from benzene in yellow crystals, which melt at 187—188°. J. J. S.

Synthesis of Indigo from Ethylenedianthranilic acid. By J. Fränkel and Karl Spiro (*Ber.*, 1895, **28**, 1685—1688).—When ethylic anthranilate (4 mols.) is heated with ethylenic bromide (1 mol.) at 140—160°, *ethylic ethylenedianthranilate*,

$$C_2H_4(NH{\cdot}C_6H_4{\cdot}COOEt)_2,$$

is formed and remains as a solid substance on treating the product with water and dilute hydrochloric acid. It crystallises from alcohol in needles melting at 117°, and is readily hydrolysed by warming with alcoholic potash. The free *ethylenedianthranilic acid* is scarcely soluble in water and only sparingly in the other neutral solvents, and crystallises from nitrobenzene in indistinct crystals, melting at 213—214°. The constitution of the acid is closely allied to that of indigo, and attempts were therefore made to convert it into the latter. The ordinary condensation agents were without effect,

but when fused with caustic potash in absence of air, according to Heumann's method, it yields a yellow mass, containing a leuco-compound which is soon converted into indigo by the oxygen of the air. The yield is, however, small. H. G. C.

Preparation of Pinacones by the Reduction of Aromatic Ketones. By K. Elbs and K. Schmitz (*J. pr. Chem.*, 1895, [2], **51**, 591—592).—The ketone was dissolved in glacial acetic acid, twice the calculated quantity of zinc dust was gradually added and the whole warmed on the water-bath until the zinc was almost entirely converted into acetate. By this treatment (1) acetone, phenylethyl methyl ketone, and dibenzyl ketone, remained unchanged; (2) acetophenone yielded the pinacone, $OH\cdot CMePh\cdot CMePh\cdot OH$; (3) benzophenone yielded benzopinacone, $OH\cdot CPh_2\cdot CPh_2\cdot OH$; (4) phenyl paratolyl ketone yielded the pinacone,

$$OH\cdot CPh(C_6H_4Me)\cdot CPh(C_6H_4Me)\cdot OH.$$

Pinacones were also obtained in this way from phenyl metaxylyl ketone, phenyl pseudocumyl ketone, phenyl α-naphthyl ketone, and, particularly easily from parahydroxybenzophenone, parethoxybenzophenone, and parahydroxybenzophenone benzoate.

A. G. B.

Orthophenobenzylamine and Cyclophenylenbenzylidene Oxide. By Paul Cohn (*Monatsh.*, 1895, **16**, 267—282).—The author has previously described the preparation of phenylorthocresolamine, $HO\cdot C_6H_4\cdot CHPh\cdot NH_2$, by the reduction of an alcoholic solution of phenylindoxazene with sodium, and on account of its close relation to orthobenzylphenol suggests for it the more appropriate name of orthophenolbenzylamine (compare this vol., i, 371). This base yields a *dibenzoyl* derivative, $C_{27}H_{21}NO_3$, which is insoluble in acids and alkalis, and an *ethyl* derivative which when freshly prepared is an oil, but gradually assumes the solid form. The latter gives a well-characterised hydrochloride and an orange-red, crystalline platinochloride, $(C_{15}H_{17}NO)_2,H_2PtCl_6$. Orthophenolbenzylamine acts as a powerful poison, is optically inactive, loses ammonia at 130—150° and when heated with dilute hydrochloric acid, first for 3—4 hours at 130—140°, and afterwards for an equal time at 150°, is resolved into ammonia and *cyclophenylenebenzylidene oxide*, $C_6H_4<\overset{CHPh}{\underset{O}{|}}$. The latter, which is obtained in 90 per cent. of the theoretical yield, crystallises from benzene in small, yellow, monoclinic needles, is insoluble in mineral acids, but dissolves readily in acetic acid or alcohol, and also in alkalis forming a brown solution. It softens at 170°, and when heated to a slightly higher temperature rapidly blackens. At 210°, it forms a dark-coloured, viscid liquid. The *benzoyl derivative*, $C_{13}H_9BzO$, is a yellow, crystalline powder, which sinters at 150°, simultaneously darkening, and at 190° becomes a thick, greasy mass. It is insoluble in acids, alkalis, alcohol, and petroleum, but dissolves in chloroform. The *ethyl* derivative, $C_{15}H_{14}O$, forms slender crystals, softens at 150°, and becomes a viscid, brown oil at 168—170°. The *acetyl* derivative, $C_{13}H_9AcO$, crystallises

from acetic acid in slender, white needles, softens and becomes yellow at 180°, and at 190° exists as a viscid, transparent fluid. The *sodium* derivative, $C_{13}H_9NaO$, is a brown powder which readily dissolves in water, to which it gives alkaline properties. G. T. M.

The Reducing Action of Alcohol at High Temperatures. By WILHELM KERP (*Ber.*, 1895, **28**, 1476).—Ethylic alcohol and amylic alcohol reduce benzophenone to benzhydrol when they are heated with it at 300—320°, the alcohols being converted into the corresponding aldehydes. The same reaction occurs with ethylic alcohol and diphenyleneketone, acetophenone, phenanthraquinone and anthraquinone. No action appears to take place at lower temperatures, and no aldehyde is formed when alcohol is heated by itself to 340°. A similar action has been observed with sodium ethoxide, at 200°, by Haller and Minguin (*Compt. rend.*, **120**, 1105). Methylic alcohol does not appear to react in this way. A. H.

Constitution of Maclurin and Phloretin. By GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1895, **28**, 1393—1398); compare Abstr., 1894, i, 471. From their own observations, and from those of König and v. Kostanecki (Abstr., 1894, i, 534), the authors think maclurin is to be regarded as 2:4:6:3′:4′-pentahydroxybenzophenone, and the condensation product obtained by the action of acetic anhydride and anhydrous sodium acetate as the tetracetyl derivative of tetrahydroxyphenylcoumarin. It is shown that maclurin is closely related to the cotoïnes, cotogenin, protocotoïn and oxyleucotin.

The substance described by Mrs. Michael (this vol., i, 45) as triacetylphloretin is shown to be a tetracetyl derivative of phloretin. A *trimethylphloretin* is obtained when phloretin is heated with methylic iodide and methylic alcoholic potash; it has the constitution

$$C_6H_2O_3Me_3\cdot CO\cdot CHMe\cdot C_6H_4\cdot OH,$$

and forms pale yellow plates which melt at 152°. When the mother liquor from this trimethyl derivative is evaporated, and the residue again treated with methylic iodide, a new substance, having the composition $C_{19}H_{22}O_5$, is obtained. This forms yellowish plates which melt at 58°. It is the methyl ether of the above mentioned trimethylphloretin, since it yields the latter when treated with hydriodic acid. J. J. S.

Phthaleïn-melts. By R. von ROTHENBURG (*J. pr. Chem.*, 1895, [2], **51**, 578—580).—The author draws a comparison between the production of fluoresceïns, rhodamines, pyronines, and fluoramines. A. G. B.

Constitution of Fluoresceïn. Ethereal Salts and Mixed Anhydride of Phthalic Acid. By RICHARD MEYER (*Ber.*, 1895, **28**, 1576—1577).—Heller has shown (this vol., i, 234) that one of the hydroxyl groups of fluorsceïn is in the para-position with respect to the carbonyl group. That the second hydroxyl group also occupies the para-position follows from the following facts. When dibromodihydroxybenzoylbenzoic acid, $COOH\cdot C_6H_4\cdot CO[C_6HBr_2\cdot(OH)_2]_2$, obtained by the action of an alkali on eosin, is heated above its melting point, it

yields phthalic acid which sublimes, and eosin; the latter is identical with the ordinary colouring matter in every respect. It follows from this that eosin, and, therefore, fluoresceïn itself must have the symmetrical constitution.

The ethereal salts obtained by acting on silver phthalate with benzylic iodide, and on sodium benzyloxide with phthalic chloride are identical. The same is true of the mixed anhydrides prepared from phthalic chloride and silver benzoate, and from benzoic chloride and silver phthalate. A. H.

Action of Iodine on Phenolphthaleïn. By ALEXANDER CLASSEN and WALTHER LÖB (*Ber.*, 1895, **28**, 1603—1611.—Phenolphthaleïn is converted by iodine into *tetraiodophenolphthaleïn*,

$$C(C_6H_2I_2\cdot OH)_2<\begin{matrix}C_6H_4\\O\end{matrix}>CO,$$

which forms yellowish, granular crystals, and decomposes at about 220° without melting. It is readily soluble in alkalis, forming salts of tetraiodophenolphthaleïncarbinolcarboxylic acid, from which the free acid, $COOH\cdot C_6H_4\cdot C(OH)(C_6H_2I_2\cdot OH)_2$, may be obtained by careful acidification at −5°. The latter is a yellowish-brown substance which is converted into tetraiodophenolphthaleïn at 100°. The *sodium salt* forms a blue mass and is soluble in water, in which tetraiodophenolphthaleïn itself is insoluble. The *barium salt* is a greyish-blue powder, whilst the salts of most of the heavy metals are brown.

Tetraiodophenolphthaleïn acts as a strong antiseptic in the animal organism, through which it appears to pass unchanged.

The preparation of the compound may be carried out by dissolving phenolphthaleïn in alkali or baryta water and adding iodine, by which means the corresponding salt is obtained. The substance itself, and not the sodium salt, is formed when phenolphthaleïn is dissolved in borax or sodium phosphate solution and treated with iodine, or when a solution of phenolphthaleïn in alkaline potassium iodide solution is submitted to electrolysis. A. H.

Sulphonated Colouring Matters of the Triphenylmethane Series. By MAURICE PRUD'HOMME (*Chem. Centr.*, 1895, i, 41; from *Bull. Soc. Ind. Mulhouse*, 1894, 400—407).—The author criticises Rosenstiehl's view that the rosanilinesulphonic acids exist in three forms; the colourless modification of acid magenta,

$$[(NH_2)(SO_3Na)C_6H_3]_3C\cdot OH,$$

is really the dye-stuff, since it contains the acid phenolic group; Rosenstiehl's supposition that a form derived from this by substituting chlorine for the hydroxyl group constitutes the colouring matter, is therefore unnecessary.

The decolorisation of patent blue can hardly be due to the conversion of the :C·OH group into the group :C·ONa, for then the colour should reappear on acidification immediately, instead of requiring several days in the cold; the colourless compound is most likely a condensation product of two molecules of the coloured one.

W. J. P.

Constitution of Acid Magenta. By AUGUSTE ROSENSTIEHL (*Chem. Centr.*, 1895, i, 41—42; from *Bull. Soc. Ind. Mulhouse*, 1894, 408—413).—The author combats the views of Prud'homme (see preceding abstract) on acid magenta. W. J. P.

Constitution of the Rosanilines. By ARTHUR MIOLATI (*Ber.*, 1895, **28**, 1696—1701).—The electrolytic conductivity of pararosaniline, as previously given by the author (Abstr., 1893, i, 572), is only half the true value, owing to an error in the calculation. The following additional determinations have been made at 25°.

	v =	128.	256.	512.	1024.
Pararosaniline	μ =	84·24	87·29	91·28	93·27
Phenosafranine.....	μ =	79·41	81·69	82·61	83·13
Methylene blue.....	μ =	88·97	93·56	95·76	96·60
Leucaniline trihydrochloride	μ =	343·9	382·4	419·9	465·3
Hydrocyanopararosaniline trihydrochloride	μ =	361·2	419·9	478·2	539·5
Pararosaniline + HCl.....	μ =	291·7	327·0	374·9	399·1
,, + 2HCl	μ =	454·8	513·6	579·4	651·6
,, + 3HCl	μ =	700·3	753·7	891·4	921·1
Hexamethylpararosaniline hydrochloride (crystal violet).....	μ =	78·0	81·60	83·88	84·71

The conductivity of pararosaniline may be dependent on the presence of amido-groups, as Rosenstiehl suggests, or may be due to its being a true salt, in the former case it should be resolved into the ions, $C_{19}H_{19}N_3Cl$ and OH, in the latter into $C_{19}H_{18}N_3$ and Cl. The maximum conductivity calculated for the first hypothesis = 190, for the second = 93·2, the close agreement of this value with the experimental results, and the analogy shown to phenosafranine and methylene blue, prove that pararosaniline is a true salt; confirmation of this is afforded by the great difference in behaviour between pararosaniline in hydrochloric acid solution, leucaniline trihydrochloride, and hydrocyanopararosaniline trihydrochloride solutions. Haller and Müller have stated that pararosaniline and crystal violet do not dissociate in aqueous solution; the author is unable to confirm this, his molecular weight determinations of the former, by the boiling point method, give values ranging from 144·8—186 (cal. = 323·7); the electrolytic conductivity of the latter is given above. By the action of hydrogen chloride on leucaniline, suspended in alcohol, a somewhat unstable compound, $C_{19}H_{19}N_3,4HCl + H_2O$, is obtained; the formation of this is incompatible with Rosenstiehl's formula, which is also not in accordance with the spectroscopic properties of pararosaniline salts; these, as Ostwald has shown, have identical absorption spectra. (Compare following abstract.)

J. B. T.

Constitution of Rosanilines. By M. TORTELLI (*Ber.*, 1895, **28**, 1702—1707).—The haloïds are completely precipitated from pararosaniline and its analogues by means of silver nitrate, in presence of nitric acid. The following compounds were examined—hydrated and

anhydrous pararosaniline, pararosaniline iodide, and "crystal violet." Barium chloride completely precipitates the sulphur of pararosaniline sulphate and "brilliant green." Full details of the experiments are given in the paper. The electrolytic conductivity of the following compounds, which resemble the ordinary pararosaniline salts, has also been determined.

	$v =$	256.	512.	1024.
Pararosaniline sulphate $(C_{19}H_{16}N_3)_2$, $H_2SO_4 + 8H_2O$	$\mu =$	83·39	85·12	86·26
Pararosaniline iodide, $C_{19}H_{16}N_3HI$.	$\mu =$	—	88·03	90·07

Müller's hydrocyanopararosaniline, $NC{\cdot}C(C_6H_4{\cdot}NH_2)_3$, is formed by the action of barium cyanide on pararosaniline sulphate, and of ammonium cyanide or hydrogen cyanide on the free base. When boiled with mercuric cyanide, in dilute alcoholic solution, pararosaniline yields a compound $C_{19}H_{17}N_3,HCl,Hg(CN)_2$, which crystallises in small, thin needles with a greenish metallic lustre, and is sparingly soluble. The corresponding *chloride*, $C_{19}H_{17}N_3,HCl,HgCl_2$, crystallises in slender plates. By the interaction of mercuric cyanide, pararosaniline, and hydrogen cyanide at 0°, two compounds are formed, the one, $C_{19}H_{17}N_3,HCN,Hg(CN)_2$, crystallises in green plates with a bronze reflex. The second substance, $2C_{19}H_{17}N_3,HCN,Hg(CN)_2$, obtained in larger quantity, is a greenish-red crystalline powder. When boiled with water, both compounds are resolved into hydrocyanopararosaniline, but they are not formed from this compound by the action of mercuric cyanide. When treated with hydrogen sulphide, mercury is eliminated from all the above double cyanides, but the solution retains the characteristic magenta colour; on evaporation, a green, crystalline compound is formed, which decomposes into the cyanopararosaniline, when attempts are made to purify it. The substance is probably the coloured cyanide corresponding with the ordinary salts of pararosaniline. The compound, $C_{19}H_{17}N_3,HCN,HgCl_2$, formed from pararosaniline, mercuric chloride, and hydrogen cyanide at 0°, is more stable than the corresponding cyanide, and is deposited in long, green, lustrous crystals. The formation of the above compounds, and the behaviour of the haloïd salts of pararosaniline, can not be explained by Rosenstiehl's pararosaniline formula (compare preceding abstract). J. B. T.

Oxidation Products of Tetramethyldiamidodiphenylcarbinol. By Auguste Rosenstiehl (*Bull. Soc. Chim.*, 1895, [3], **13**, 273—275).—Tetramethyldiamidodiphenylcarbinol,

$$OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2,$$

is oxidised by sulphuric acid at 125° to the corresponding ketone, but by lead peroxide in presence of hydrochloric acid to tetramethylbenzidine, $NMe_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMe_2$, with elimination of carbonic anhydride. A noteworthy point in the latter oxidation is the stability of the dimethylamidophenyl groups. Jn. W.

Instability of Tetramethyldiamidodiphenylcarbinol. By Auguste Rosenstiehl (*Bull. Soc. Chim.*, 1895, [3], **13**, 275—277).—

The author confirms his previous results, and in commenting on the subsequent results obtained by Weil (this vol., i, 145), shows that the decomposition of this carbinol by acids into hexamethyltriamidotriphenylmethane and paradimethylamidobenzaldehyde is practically quantitative, and takes place to a certain extent even in the cold, and in dilute solutions. JN. W.

Iodine Green. By LÉON LEFÈVRE (*Bull. Soc. Chim.* 1895, [3], **13**, 247—252).—In dyes of the rosaniline type, the effect on the colour produced by neutralising a para-amido-group is the same as that of eliminating it, violet becoming green, and green red. As this first colour change takes place in the formation of iodine green from the violet-red colouring matter, $CI(C_6H_4\cdot NHMe)_2\cdot C_6H_3Me\cdot NHMe$, the methylic iodide must have transformed an amido into an ammonium group, and the constitution of the green dye must therefore be

$$CI(C_6H_4\cdot NHMe)_2\cdot C_6H_3Me\cdot NMe_3I,H_2O.$$

A substance having this constitution would, as Hofmann found, readily lose water and methylic iodide, and the product of this decomposition would have the constitution $CI(C_6H_4\cdot NHMe)_2\cdot C_6H_3Me\cdot NMe_2$, and, therefore, be bluer in tinge than the corresponding trimethyl compound, as is the case. The composition and constitution usually assigned to iodine green by analogy with hexamethylpararosaniline, namely, $CI(C_6H_4\cdot NMe_2)\cdot C_6H_3Me\cdot NMe_3I$, do not account for the formation of a violet colouring matter having the above composition, and, moreover, are not in accordance with Hofmann's analytical data.

In accordance with these views, the violet colouring matters prepared by Hofmann and Girard by heating iodine green with methylic alcohol, would have the constitutions

$$NMe_2\cdot C_6H_4\cdot CI(C_6H_4\cdot NMe_2HI)\cdot C_6H_3Me\cdot NMe_2HI,$$

and $CI(C_6H_4\cdot NHMe)\cdot C_6H_3Me\cdot NMe_2$, respectively, and the colourless product obtained at the same time, the constitution

$$NMe_2HI\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_3I)\cdot C_6H_3Me\cdot NMe_3I,H_2O.$$

JN. W.

A Synthesis of Unsaturated Aromatic Acids. By GEORG HEYL and VICTOR MEYER (*Ber.*, 1895, **28**, 1798—1799).—*Triphenylacrylonitrile*, $CPh_2{:}CPH\cdot CN$, can be obtained by heating benzophenone chloride, CPh_2Cl_2, with benzylic cyanide in an open vessel until the evolution of hydrogen chloride ceases; it crystallises in needles and melts at 162—163°. It cannot be hydrolysed to the acid in the usual manner; prolonged boiling with alcoholic potash, however, converts it into the *amide*, melting at 223°, and this can be further converted into the *acid* by treatment with sodium nitrite and sulphuric acid. The acid may also be prepared by heating benzophenone chloride with ethylic phenylacetate, and hydrolysing the ethylic salt thus obtained with alcoholic potash; it crystallises in needles, and melts at 212—213°. C. F. B.

Triphenylthienylmethane. By KARL WEISSE (*Ber.*, 1895, **28**, 1537—1538).—*Triphenylthienylmethane*, $C_4SH_3{\cdot}CPh_3$, is prepared by heating triphenylcarbinol and thiophen with phosphoric anhydride; it crystallises from a mixture of benzene and light petroleum in needles or large prisms, melts at 239°, and boils at 433—438° (corr.), a small portion being decomposed. The yield is quantitative. The formation of this compound shows that the failure of all attempts to prepare tetraphenylmethane is due either to the comparatively great stability of benzene or to its own instability, and not to any stereochemical cause, since the volume occupied by the thienyl and phenyl groups is practically equal. J. B. T.

Oxidation of Nitronaphthalene. By PAUL FRIEDLAENDER and J. WEISBERG (*Ber.*, 1895, **28**, 1641—1643).—When nitronaphthalene is oxidised by boiling with aqueous permanganate solution, and the filtrate reduced with ferrous sulphate, ethylic acetate extracts two substances from the colourless solution thus obtained. That one which first crystallises appears to be *isatincarboxylic acid*, $C_9H_5NO_4$; it turns brown above 200°. It yields a *barium salt* in yellow needles, and the solution of this salt is turned cherry-red by the addition of baryta water; on warming, the colour changes to pale yellow, and the addition of acids also restores the original reddish-yellow colour. The acid can further be converted into indopheninecarboxylic acid, and also into indigocarboxylic acid. C. F. B.

Reaction of 1 : 3 : 1′-Nitronaphthalenedisulphonic acid. By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1535—1537).—1 : 3 : 1′-Nitronaphthalenedisulphonic acid is formed from 1 : 3′-naphthalenedisulphonic acid, and is employed for the technical preparation of 1 : 3 : 1′-naphtholdisulpponic acid (ε-acid). The *potassium salt*, $C_{10}H_5NO_2(SO_3K)_2$, and the *calcium salt* crystallise in yellow needles; the *barium salt* is deposited in flat, stellate needles; the *zinc salt* in long, thin, almost colourless, crystals; the *lead* and *copper* salts have also been prepared, all are readily soluble. When carefully heated with soda, the above potassium salt is converted into the basic sodium salt of 1-*nitroso*-4-*naphthol*-3 : 1′-*disulphonic acid*, which crystallises in slender, greenish, lustrous needles; the *potassium salt*,

$$C_{10}H_5NO_2(SO_3K)_2 + 1{\cdot}5H_2O,$$

is deposited in small, yellow, stellate needles; the *basic potassium salt* forms green needles, the basic and neutral *calcium* and *barium salts* also crystallise in needles; all are readily soluble. When reduced the above compound is converted into 1 : 4-*amidonaphthol*-3 : 1′-*disulphonic acid*, which crystallises in colourless needles, can not be diazotised, does not combine with diazo-compounds, and, in alkaline solution, turns green when exposed to air. The *silver salt* is pale yellow and insoluble; the *potassium*, *barium*, and *copper salts* are readily soluble. By the action of sodium amalgam on the above acid in neutral or slightly acid solution, one sulphonic group (probably that in the 1′ position) is eliminated, the resulting compound crystallises in silvery, lustrous plates, and, when further reduced, yields

1 : 4-amidonaphthol. The formation of the nitrosonaphthol resembles the intramolecular rearrangement which occurs in the case of phenylhydroxylamine derivatives; none of the isomeric nitronaphthalenesulphonic acids that have hitherto been investigated undergo a similar change. J. B. T.

Constitution of β-Anthraquinone. By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 1422—1424).—The β-anthraquinone (Abstr., 1894, i, 420) obtained by the author from 2-hydroxyanthracene was previously shown to be an orthoanthraquinone, and is now shown to be the 1 : 2-anthraquinone.

When the nitroso-derivative of 2-hydroxyanthracene is treated in alkaline solution with hydrogen sulphide, free *amidohydroxyanthracene* is obtained; this, on recrystallisation from ether, forms greenish-yellow plates, which, when quite pure, are not decomposed on exposure to the air. They darken at 140°, and decompose at 150°. A *triacetyl derivative*, $OAc{\cdot}C_{14}H_8{\cdot}NAc_2$, was prepared by warming the amidohydroxyanthracene for a short time with acetic anhydride; after recrystallisation from dilute alcohol, it forms large, slightly fluorescent plates, which melt at 164°. When oxidised with chromic acid, it yields *triacetylamidohydroxyanthraquinone*, $OAc{\cdot}C_{14}H_6O_2{\cdot}NAc_2$, which crystallises from benzene in bright yellow, flat prisms, and melts at 181°. This triacetyl compound may be hydrolysed by prolonged boiling with a solution of sodium hydroxide; when the blood-red solution thus obtained is acidified, a deep red precipitate of hydroxyamidoanthraquinone is thrown down. This compound is identical with the alizaramide of Liebermann (this Journal, 1877, i, 613), which has the constitution 1 : 2-amidohydroxyanthraquinone. It therefore follows that the original hydroxyamidoanthracene is 1 : 2-amidohydroxyanthracene. As the β-anthraquinone is obtained by the oxidation of this 1 : 2-amidohydroxyanthracene, it follows that it is the 1 : 2-anthraquinone. J. J. S.

2 : 3-Dihydroxyanthracene. By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 1533—1535).—2 : 3-*Dimethoxyanthracene* is readily prepared by the action of zinc dust and dilute ammonia on hystazarin dimethyl ether (this vol., i, 232); it crystallises from petroleum in colourless plates, melts at 203—204°, and, in alcoholic solution, exhibits a fluorescence similar to that of anthracene, which it resembles in appearance. The yield is quantitative. The compound sublimes when slowly heated; in solution, it gradually changes both in melting point and appearance, polymeric compounds being probably formed. The *picrate* is dark brown, and readily soluble.

2 : 3-*Dihydroxyanthracene*, formed by the action of hydriodic acid on the preceding compound, is deposited with some difficulty in pale yellow, ill-developed crystals; it chars without melting, and dissolves in sulphuric acid with a brownish-red coloration; when heated, th colour changes to dull green, then to blue. The compound is not oxidised by heating with ferric chloride, platinum tetrachloride, gold chloride, or chromic acid, boiling dilute nitric acid decomposes it, but is without action at the ordinary temperature; the product

formed by treatment with potassium ferricyanide was ill defined; this indicates that the substance is a diphenol, not a quinol, and that the carbon atoms 2:3 are probably singly linked. The *diacetyl derivative* is deposited in small, pale yellow, concentric crystals, melting at 160°. In solution, it shows a faint fluorescence, resembling that of anthracene. J. B. T.

Synthesis of Alizarin from Hemipinic acid. By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 1427—1429).—The author has previously shown (*Ber.*, **27**, 116) that when phthalic anhydride is treated according to Friedel-Craft's method with an ether of quinol or of catechol, the products are respectively quinizarin and hystazarin. The action of benzene on hemipinic acid in the presence of aluminium chloride has since been studied; the product obtained by decomposing the resulting aluminium compound with hydrochloric acid crystallises in long, colourless needles, and melts at 86—87°; it has the composition $C_{15}H_{12}O_5 + H_2O$, and is probably a *hydroxymethoxybenzoylbenzoic acid*, its formation being due to the hydrolysis of one of the methoxy-groups of hemipinic acid by the aluminium chloride. It dissolves in cold concentrated sulphuric acid, yielding a yellowish-red solution with a yellowish-green fluorescence. If this solution is heated to 100°, the colour changes to dark red and then to violet; when the latter solution is poured on to ice, a precipitate of a monomethyl ether of alizarin is obtained. This ether crystallises from glacial acetic acid in long, glistening, reddish-yellow needles, which melt at 201°; it is only partially hydrolysed when heated with concentrated hydrochloric acid at 100—150°, and is very stable towards concentrated potash, but is readily hydrolysed when heated for a short time with hydriodic acid (b. p. 127°). The synthetical alizarin thus obtained melted at 260°, whereas pure alizarin melts at 289°. The low melting point is probably due to a small quantity of the methyl ether contained in the specimen. J. J. S.

Finland Turpentine. By OSSIAN ASCHAN and EDVARD HJELT (*Chem. Zeit*, 1894, **18**, 1566—1567).—Three samples of turpentine were examined: 1. Turpentine from South Finland. This was prepared from fir roots (*Pinus Abies*); after repeated distillation, the following fractions were obtained: 155—160° = 7·1; 160—165° = 30·2; 165—170° = 22·6; 170—175° = 20·1 per cent. The lowest fraction contained pinene. The others were redistilled, the portion boiling at 170—174° contained sylvestrene and dipentene, the remainder (b. p. 174—178°) contained dipentene but no sylvestrene. This turpentine is therefore similar in composition to Swedish and Russian. 2. Turpentine from North Finland. Prepared partly from wood tar and partly from pine wood, the fractions 160—165° and 165—170° were small, 170—174° = 32·2; 174—178° = 21·5 per cent., the former contained pinene, the latter dipentene and probably sylvestrene. 3. Turpentine prepared by the distillation of resinous wood with steam. The chief fraction, = 50 per cent., boiled at 155—156°, and contained much pinene, the higher boiling portions contained sylvestrene but no dipentene, proving that the former compound is

contained in the wood, and that the latter is formed, during the distillation, from pinene. When treated with nitric acid, the lower fractions containing pinene yield, chiefly, terebic acid, whilst the higher fractions containing dipentene give terephthalic acid. The various terpenes were isolated and identified by the preparation of their hydrochlorides and nitroso-derivatives. J. B. T.

Limonene Nitrosochloride. By Otto Wallach (*Ber.*, 1895, **28**, 1474).—The results of the determination of the molecular weights of the two nitrosochlorides quoted in a previous paper (this vol., i, 478) are falsified by an error in the calculation. In phenol solution, both the α- and β-nitrosochloride have the bimolecular formula, so that the β-compound has the same molecular weight in solution in phenol and in benzene. A. H.

Compounds of the Carvacrol and Thymol Series. By Otto Wallach and Franz Neumann (*Ber.*, 1895, **28**, 1660—1665).—Carvacrylamine may be obtained by the action of potash on isocarvoxime as well as on carvoxime (Abstr., 1894, i, 536); the isocarvoxime employed was prepared by the elimination of hydrogen bromide from hydrobromocarvoxime, the latter being found by the authors, in agreement with Goldschmidt (Abstr., 1887, 903), to melt at 116°, whereas Baeyer (Abstr., 1894, i, 298) gives the melting point as 136°; it is probable that two different hydrobromocarvoximes are formed under the varying conditions of the reaction.

Amidocarvacrol, $NH_2 \cdot C_{10}H_{12} \cdot OH$, is formed by the reduction of nitrosocarvacrol with tin and hydrochloric acid, the nitroso-derivative being prepared by the action of sodium ethoxide and amylic nitrite on carvacrol. The amido-compound is isolated in the usual manner as the *hydrochloride*; the latter forms thick prisms melting at 214—215°, and, on careful treatment with ammonia, yields the free base as a readily oxidisable precipitate, which separates from methylic alcohol in colourless crystals melting at 134°, and, on oxidation, yields thymoquinone. When boiled with acetic anhydride and anhydrous sodium acetate, it yields *triacetylamidocarvacrol*, $C_{10}H_{12}(NAc_2)OAc$, which, after crystallisation from light petroleum, melts at 75·5°, and, on boiling with the requisite amount of aqueous soda, yields *acetylamidocarvacrol*, $NHAc \cdot C_{10}H_{12} \cdot OH$, a crystalline compound melting at 176—177°. On methylation, it is converted into the *methylic ether*, $NHAc \cdot C_{10}H_{12} \cdot OMe$, crystallising in slender needles and melting at 140°; when boiled with hydrochloric acid, the latter loses the acetyl group, forming the hydrochloride of *amidocarvacrol methyl ether*, $NH_2 \cdot C_{10}H_{12} \cdot OMe$, which crystallises in needles melting at 229°, readily oxidises, and with ferric chloride gives a blue coloration. On acetylation, it forms the *diacetyl derivative*, $C_{10}H_{12}(NAc_2) \cdot OMe$, which crystallises in slender needles and melts at 104°.

Amidothymol, $NH_2 \cdot C_{10}H_{12} \cdot OH$, is obtained by the reduction of nitrosothymol, and is identical in all respects with the substance obtained by the action of sulphuric acid on carvoxime. Its *hydrochloride* begins to turn brown at 240°, and melts at 255°. Like amidocarvacrol, it yields a *triacetyl* derivative, which crystallises in

plates and melts at 91°. The *monacetyl* compound melts at 174·5°, and its *methylic ether* at 139°; the *hydrochloride* of *amidothymol methyl ether*, $NH_2 \cdot C_{10}H_{12} \cdot OMe,HCl$, obtained by boiling the latter with hydrochloric acid, crystallises in long needles, melts at 250° with decomposition, and gives a blue colour with ferric chloride solution.

The only bromocarvacrol hitherto described is a liquid (Mazzara, *Gazzetta*, **16**, 194), but a crystalline preparation may be obtained by acting on carvacrol with bromine in acetic acid solution; it melts at 46° and boils at 162—163° under 12 mm. pressure. It yields an oily *acetyl* derivative and *methylic ether*, the latter boiling at 147—150° under 15 mm. pressure. H. G. C.

Constitution of Terpineol. By Otto Wallach (*Ber.*, 1895, **28**, 1773—1777; compare following abstract).—The exact constitution of terpineol, although of such great importance, in view of the close relationship of this compound with so many other compounds of the terpene series, has not yet been proved, the position of the ethylene linking and the hydroxyl being still uncertain. The author has recently shown (this vol., i, 59) that it may be converted by a series of reactions into carvone, in which the ethylene linking is in the Δ1 position, but in these reactions the possibility of intramolecular change was not excluded. Further research has shown, however, that the same change may be effected by acting on terpineol nitrosochloride with hydrochloric acid, which converts it into a *hydroxyoxime*, $OH \cdot C_{10}H_{15} \cdot NOH$, melting at 134°; this compound, when boiled with dilute acids, loses water and hydroxylamine, yielding a mixture of carvacrol and inactive carvone. It is very improbable that intramolecular change would take place in these reactions, and it may therefore be concluded that in terpineol the ethylene linking is in the Δ1 position.

With regard to the position of the hydroxyl group, the author has already shown (Abstr., 1894, i, 43) that, on oxidation, terpineol yields two compounds having the composition $C_{10}H_{20}O_3$ and $C_{10}H_{16}O_3$; the former, under suitable conditions, loses 3 mols. H_2O, forming cymene, and must therefore be a trihydroxyhexahydrocymene, two of the hydroxy-groups being in the 1 : 2 position, whilst the third must occupy the same position as the hydroxyl group in terpineol, which is usually assumed to be the 4-position. Against this supposition is the fact that terpineol yields terpenylic acid on oxidation, which is not readily understood if it contains the group $\cdot C(OH) \cdot CHMe_2$, but would readily follow if the hydroxyl were in the side chain giving the group $\cdot CH \cdot C(OH)Me_2$. As terpineol is a tertiary alcohol, no other position of the hydroxyl group is possible, and it therefore remains to distinguish between the formulæ

$$CMe\begin{matrix}<\\>\end{matrix}\begin{matrix}CH \cdot CH_2\\CH_2 \cdot CH_2\end{matrix}\begin{matrix}>\\<\end{matrix}C(OH) \cdot CHMe_2 \text{ and}$$

$$CMe\begin{matrix}<\\>\end{matrix}\begin{matrix}CH \cdot CH_2\\CH_2 \cdot CH_2\end{matrix}\begin{matrix}>\\<\end{matrix}CH \cdot C(OH)Me_2.$$

In order to do this, the second of the above oxidation products,

having the formula $C_{10}H_{16}O_3$, was examined, and found to be a ketone, as it yields an *oxime*, melting at 76—77°, and a *semicarbazone*, melting at 200°. It also contains a lactone group, and on treatment first with soda and then with silver solution, yields the silver salt of an acid, $C_{10}H_{18}O_4$. It yields, as previously stated, terpenylic acid and acetic acid on oxidation, and on treatment with bromine in alkaline solution yields the same acid, together with bromoform or carbon tetrabromide. Hence it must be derived from terpenylic acid by the displacement of carboxyl by the group $CH_2{\cdot}COMe$. The most probable constitution of terpenylic acid is $\begin{matrix}O\text{—}CMe_2\\ |\\ CO{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}CH_2{\cdot}COOH$ (compare *Annalen*, **259**, 322; Schryver, this Journ., 1893, 1327; Wolff, *Inaug. Diss.*, Strasburg, 1894), and in that case the constitution of the above ketolactone must be $\begin{matrix}O\text{—}CMe_2\\ |\\ CO{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, and the hydroxyl group in terpineol must be in the side chain, as shown by the second of the two formulæ given above. It is, however, possible, by assuming a number of intermediate reactions, to explain the conversion of terpineol into the ketolactone on the assumption of the first formula, and the former cannot therefore be yet regarded as absolutely disproved, although it is the less probable. If the new formula proves to be correct, many of the conclusions as to the orientation of compounds in the terpene series will have to be modified. H. G. C.

Methoethylheptanonolide. By FERDINAND TIEMANN and F. W. SEMMLER (*Ber.*, 1895, **28**, 1778—1781).—By the oxidation of pinene, the authors obtained, together with pinonic acid, a substance having the formula $C_{10}H_{16}O_3$ (this vol., i, 477).—This compound is not, however, formed from pinene, but from an impurity contained in commercial pinene; it forms crystals melting at 63—64°, and is identical with the compound $C_{10}H_{16}O_3$, obtained by Wallach (see previous abstract) by the oxidation of terpineol. The authors have determined its constitution in almost the same manner as Wallach, and have arrived independently at the same constitutional formula, according to which it is *methyl-3′-ethyl-3-heptanon-6-olide-1-3′*. Like Wallach, they regard this as showing that in terpineol the hydroxyl group is in the side chain. H. G. C.

Oxidation of Terpin, Terpin Hydrate, and Terpineol. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1895, **28**, 1781—1784).—Solid terpineol may be readily and quantitatively converted into terpin hydrate by mixing it with a little benzene and shaking the whole with 100 parts of 5 per cent. sulphuric acid for about five days. Liquid terpineol is also converted into terpin hydrate in the same manner, but 8—10 days are required for its complete conversion, and sufficient cineol is formed to be detected by its odour.

Terpin is converted by chromic anhydride, in acetic acid solution and in absence of water, into an orange compound, which explodes at 150°, and when warmed in acetic acid solution yields, together with re-formed terpin hydrate, the methoethylheptanonolide described in

the previous abstract. Terpin hydrate is not acted on by potassium permanganate at the ordinary temperature, but, on warming, it is completely resolved into simple compounds, such as acetic acid, oxalic acid, &c. From this behaviour it is probable that terpin hydrate is an open chain compound, the addition of the elements of water to terpin, which is usually represented as a dihydroxyhexahydrocymene, causing the opening of the closed chain at a point not yet determined.

The examination of the products of oxidation of solid terpineol has led to results in full agreement with those obtained by Wallach (see preceding abstracts). Liquid terpineol gives, in general, the same products on oxidation as the solid compound, although slight differences have been observed. Whether these differences are due to the fact that the two compounds are stereoisomeric, or whether the liquid terpineol contains small quantities of a structurally isomeric impurity, has not yet been determined. H. G. C.

Some Derivatives of Menthol and of Menthene. By IVAN KONDAKOFF (*Ber.*, 1895, **28**, 1618—1621).—Arth's conclusion (Abstr., 1886, 892) is confirmed, that the menthylic chloride obtained by the action of phosphoric chloride on menthol is identical with the menthene hydrochloride obtained by the direct addition of hydrogen chloride to menthene. Further, menthylic bromide and menthene hydrobromide were each prepared in two ways, and the products in all four cases were identical; they boiled at 100—103° under 13 mm. pressure, and had a sp. gr. = 1·174—1·186 at 0° = 1·155—1·166 at 23°. This identity is contrary to what is to be expected, if we assume the correctness of the commonly accepted formula for menthene, and of the laws usually supposed to govern the addition of halogen acids to unsaturated compounds. C. F. B.

Orientation in the Terpene Series. Constitution of Carone. By ADOLPH BAEYER (*Ber.*, 1895, **28**, 1586—1603; compare Abstr., this vol., i, 379).—In order to obtain an insight into the nature of the products formed by the action of hydrogen chloride on bisnitrosocarone, which are caronebisnitrosylic acid and a chlorinated ketone, the same reaction has been applied to the derivatives of menthone and tetrahydrocarvone. Bisnitrosomenthone (Abstr., 1894, i, 522) reacts with alcoholic hydrogen chloride in the same way as bisnitrosocarone, and, if the products be rapidly removed, *menthonebisnitrosylic acid* may be obtained as a crystalline mass, whilst the *monochloromenthone* is an oil. If the products are left too long in contact with the alcoholic hydrogen chloride, decomposition occurs, and menthone is formed.

Since the nitroso-group always enters the molecule in the α-position relatively to the ketone group, and in this case is combined with a tertiary carbon atom, it follows from the constitution of menthone that the monochloromenthone formed has the formula

$$CPrCl<\begin{matrix}CH_2\cdot CH_2\\ CO\ CH_2\end{matrix}>CHMe.$$

It is not identical with hydrochloropulegone, and on distillation with sodium acetate and acetic acid gives an unsaturated ketone, apparently identical with that prepared by Kremers (Abstr., 1894, i, 468) from menthene nitrosochloride.

Bisnitrosotetrahydrocarvone yields *tetrahydrocarvonebisnitrosylic acid*, whilst *monochlorotetrahydrocarvone*, $CPrH<^{CH_2\cdot CH_2}_{CH_2\cdot CO}>CMeCl$, yields an unsaturated ketone, which is not identical with carvotanacetone, since the *semicarbazide compound* melts at 224°, whilst that of carvotanacetone melts at 177—179°. This substance will be further described.

Carone combines with hydrogen bromide to form the hydrobromide of dihydrocarvone, and it is therefore important to know the constitution of the latter. Dihydrocarveol hydrobromide, when treated with silver acetate, yields an oil, which on hydrolysis is converted into a *glycol*, $C_{10}H_{18}(OH)_2$; this crystallises in slender, white needles, melting at 110·5—112°. This glycol is attacked by hydrobromic acid in the cold, forming a heavy oil, and therefore contains a tertiary hydroxyl group. Hence the bromine atom which has been displaced by hydroxyl must have been combined with a tertiary carbon atom, since the hydroxyl group of dihydrocarveol is a secondary one. The glycol is converted by oxidation into a ketone, the *semicarbazide compound* of which crystallises in large prisms, and melts at 139°.

Dihydrocarvone hydrobromide, when treated with silver acetate, yields an oil, which by hydrolysis and treatment with sodium and alcohol is converted into the glycol just described. The bromine atom of dihydrocarvone hydrobromide must therefore have the position 4 or 8, and, although it has hitherto been found impossible to definitely settle the question, it appears most probable that it has the position 4. A hydrobromodihydrocarvone of the formula

$$CHMe_2\cdot CBr<^{CH_2\cdot CH_2}_{CH_2\cdot CO}>CMeH\ [Br = 4]$$

can yield three dihydrocarvones, whilst if the formula be

$$CBrMe_2\cdot CH<^{CH_2\cdot CH_2}_{CH_2\cdot CO}>CMeH\ [Br = 8],$$

only one dihydrocarvone can result.

When *i*-hydrobromodihydrocarvone is distilled with sodium acetate and acetic acid, a mixture of two ketones, dihydrocarvone and carvenone, is formed, a reaction which clearly shows the close relation between these two substances. When the hydrobromide is treated with silver acetate, an oil is formed, which is coloured blue by sodium nitrite and hydrochloric acid, and is probably the third ketone. It is, however, very unstable, and decomposes when distilled.

The fact that alcoholic substances containing the 4 : 8 double linking form blue nitrosochlorides, whilst dihydrocarveol does not, seems to show that the latter, and therefore also dihydrocarvone, does not contain a 4 : 8 double linking, so that the double linking of dihydrocarvone must be in the ring, and the bromine atom can only enter the position 4. Dihydrocarveol and its derivatives yield hydrobromides

which can be converted into very unstable substances, which probably do contain the 4 : 8 double linking, and form blue nitrosochlorides, an additional proof that this linking is absent from dihydrocarveol itself.

1-*Bisnitroso*-4-*bromotetrahydrocarvone*, prepared from 1-dihydrocarvone, crystallises in rhombic tablets which melt and decompose at 131°. The corresponding *derivative of* i-*dihydrocarvone* melts at 140°. The corresponding *chloro-derivative of* i-*dihydrocarvone* forms small needles, and melts at 142°; this last substance is decomposed by alcoholic hydrogen chloride, with formation of i-*dichlorodihydrocarvone*, which crystallises in almost rectangular tablets melting at 66—68°. This compound is identical with the substance formed by the action of alcoholic hydrogen chloride on bisnitrosocarone, prepared from *i*-carvone. *i*-Dibromodihydrocarvone is formed by the action of alcoholic hydrogen chloride on *i*-bisnitrosobromotetrahydrocarvone, and is identical with the product obtained in a similar manner from the bisnitrosocarone prepared from *i*-carvone. The same compound has also been obtained by Wallach from dihydrocarvone by the action of hydrobromic acid and bromine.

a-*Dichlorodihydrocarvone* crystallises in colourless needles melting at 42°. *a*-Dibromodihydrocarvone, which crystallises in tablets melting at 96—97°, is formed from bisnitrosocarone, and has also been prepared by Wallach from dihydrocarvone. The various modes of formation of these compounds show that the halogen atoms in them must have the position 1 : 4.

Since the bisnitroso-compound of 4-chlorotetrahydrocarvone is converted by hydrogen chloride into the same 1 : 4-dichlorotetrahydrocarvone as is obtained from bisnitrosocarone, it follows that the nitroso-group of the latter, and therefore the hydrogen atom in carone, must occupy position 1. The formula for carone is therefore most probably $CPr\begin{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\\ CH_2\cdot CO\end{matrix}\end{>}CH$, since any other possible arrangement would involve the presence of a trimethylene ring.

The presence of a methylene group adjacent to a keto-group may be proved in compounds of the terpene series by converting them into a hydroxymethylene compound by the action of an ethereal formate, decomposing this with dilute alkali, and showing that the substance regained is identical with the original ketone. Treated in this way, carone undergoes reduction to tetrahydrocarvone, which is therefore regained instead of the original carone. The *semicarbazide compound of* a-*tetrahydrocarvone* crystallises in prisms melting at 194—196°.

The substance previously (this vol., i, 380) described as carone-bisnitrosone proved to be simply impure bisnitrosocarone.

A. H.

Essence of Cananga. By Albert Reychler (*Bull. Soc. Chim.*, 1895, [3], **13**, 140—142; compare this vol., i, 425).—The essence, after hydrolysis with potash and distillation with steam, yielded an oil boiling at 170—210°, and this, when reduced with sodium, was resolved into a volatile oil and an alkylic oxide. The *alcohol* from the

latter possessed the properties of linaloöl, $C_{10}H_{18}O$; it boiled at 193—200°; its sp. gr. = 0·8751 at 15·5°, and the refractive index is 1·46920 at the same temperature, whence the molecular refraction = 48·86°. Part of the *volatile oil* boiled at 171—175°, and approximated in composition to that required by the formula $C_9H_{12}O$; sp. gr. = 0·9325; refractive index = 1·49702. It was probably either paramethoxytoluene or paramethoxyethylbenzene, as it yielded anisic acid on oxidation. JN. W.

Camphoric Acid. By WILLIAM A. NOYES (*Amer. Chem. J.*, 1895, **17**, 421—434).—This paper consists of a detailed account of the investigation summarised in this vol., i, 295.

The depression of the freezing point of acetic acid by cis-campholytic acid establishes the molecular formula $C_8H_{13}\cdot COOH$ for the acid, and Walker has privately informed the author that the ethylic salt of "camphothetic acid" has the molecular weight 182; hence the identity of the two acids is proved. A. G. B.

The Products of Oxidation of Camphoric acid. By LUIGI BALBIANO (*Ber.*, 1895, **28**, 1506—1508; compare Abstr., 1894, i, 614).—The bibasic acid, $C_{18}H_{14}O_4$, obtained by the reduction of the acid, $C_8H_{12}O_5$, is converted by oxidation into asymmetric dimethylsuccinic acid, and is probably *αββ-trimethylglutaric acid*,

$$COOH\cdot CHMe\cdot CMe_2\cdot CH_2\cdot COOH,$$

since it cannot be converted into the known dimethylethylsuccinic acid, melting at 139°, and when heated with acetic chloride, yields an anhydride which crystallises in interpenetrating plates, and melts at 80—81°.

The acid, $C_8H_{12}O_4$, which accompanies the one just mentioned, is a monobasic lactonic acid, and forms a *silver salt*, $C_8H_{11}O_4Ag$, and a crystalline *barium salt*, $(C_8H_{11}O_4)_2Ba,4H_2O$. When heated with alkalis, the corresponding hydroxy-acid is formed, the *silver salt* of which, $C_8H_{12}O_5Ag_2$, is a white crystalline precipitate. On heating the lactonic acid with sulphuric acid, carbonic anhydride is evolved, but the acid formed has not yet been obtained in quantity sufficient for examination. A. H.

Campholenic acid and Campholenamides. By AUGUSTE BÉHAL (*Compt. rend.*, 1895, **120**, 927—930).—The campholenamide melting at 86—87° is obtained by heating camphoroxime at 100° with twice its weight of hydrogen chloride in aqueous solution, and heating the nitrile with alcoholic potash.

The amide melting at 130·5° is obtained from the nitrile formed by the action of slightly more than the calculated quantity of acetic chloride or thionyl chloride on camphoroxime. It crystallises from alcohol of 60° in prismatic needles, and is probably identical with the amide already known and described as melting at 124—127°.

The amide melting at 106° is obtained from the nitrile which is formed, if, after the action of the acetic chloride on the oxime has ceased, the product is heated at 100° for about 10 minutes. If the

heating is more prolonged, the resulting nitrile yields the amide melting at 92°.

The amide which melts at 106° forms large lamellæ and its melting point is not altered by repeated crystallisation from water or toluene. On hydrolysis, it yields two campholenic acids, one of which melts at 50°, whilst the other is a liquid boiling at 152° under a pressure of 13 mm. If, however, the amide is repeatedly crystallised from twice its weight of alcohol of 60°, it splits up into the amides melting at 130·5° and 86° respectively and hence seems to be a molecular combination of the two. In a similar manner the amide that melts at 92° can be split up into those melting at 130° and 86°.

It would seem, therefore, that there are really only two campholenamides, one melting at 130·5°, and the other at 86°. The former is converted into the latter by heating with hydrochloric acid in presence of dilute alcohol.

In presence of benzene, the amide melting at 130·5°, combines with 2 mols. of hydrogen iodide (owing to the presence of an ethylenic as well as an amido-group), and if the product is treated at once with an alkali the original amide is regenerated, but if it is allowed to remain exposed to the air for not less than 48 hours, and is then heated with an alkali, it yields the amide melting at 86°, together with campholenolide, which boils at 258° under a pressure of 760 mm., and exists in both a gelatinoïd and a well-crystallised form, which melt at the same temperature, 30°.

When the liquid campholenic acid is converted into the ethylic salt by the action of hydrogen chloride in presence of alcohol, the solid acid is obtained on hydrolysis, but if the ethylic salt is formed by the action of ethylic iodide on the sodium salt, it regenerates the liquid acid when hydrolysed.

The ammonium salt of the solid acid, when heated at 280°, yields the amide melting at 86°, whereas the liquid acid as Goldschmidt and Zurrer have shown, yields the amide melting at 130·5°.

The liquid acid and its nitrile and amide are optically active, whereas the solid acid and its derivatives are not, and hence it would seem that the solid acid is a racemic form of the liquid. Attempts to resolve the former into two optically active forms by crystallisation of the strychnine and cinchonine salts were unsuccessful, and if the action of moulds also gives negative results it will follow that the isomerism of the liquid and solid campholenic acids is analogous to that of fumaric and maleic acids (compare this vol., i, 241).

C. H. B.

New Glucoside allied to Amygdalin. By Emil Fischer (*Ber.*, 1895, **28**, 1508—1513).—Amygdalin is regarded by H. Schiff (*Annalen*, 1870, **154**, 337) as a derivative of benzaldehyde cyanhydrin with a disaccharide. The nature of this disaccharide is unknown; the author believes, however, that amygdalin is a derivative of maltose or of a similarly constituted diglucose, and for the following reasons. When amygdalin is submitted to the action of yeast extract, in presence of toluene, at 35° for seven days, half the sugar residue is split off as glucose (compare this vol., i, 7), without

the nitrogenous portion of the molecule being attacked. Under these conditions there is obtained a glucoside—*benzalnitrile glucoside*, $CN\cdot CHPh(O\cdot C_6H_{11}O_5)$, which closely resembles amygdalin. It crystallises from hot chloroform, of which it requires 2000 parts for dissolution, in colourless needles, sinters together at 140°, and melts at 147—149°. Its specific rotatory power at 20° (c. = 8—9) is $[\alpha]_D = -26{\cdot}7°$; the bitter taste is more pronounced than that of amygdalin. Boiled with alkali, ammonia is evolved, and a product formed which is probably analogous to amygdalinic acid. The new glucoside yields glucose when warmed with 5 per cent. hydrochloric acid, and when treated with emulsin, glucose, benzaldehyde, and hydrogen cyanide are formed. Since amygdalin is tolerably disseminated in the vegetable kingdom, the new glucoside may also occur in nature; and it may, perhaps, be found possible to isolate it from the apparently impure preparation described as "amorphous amygdalin" or "laurocerasin" (Lehmann, *Neues Rep. f. Pharm.*, **23**, 449).

A. R. L.

Quercetin Derivatives. By Josef Herzig (*Monatsh.*, 1895, **16**, 312—320; compare Abstr., 1888, 1309; 1890, 64; 1891, 1386; 1893, i, 413).—The author reviews his previous work on quercetin derivatives and on the constitution of quercetin, and in opposition to Liebermann (this vol., i, 429), still maintains that it is represented by the formula $C_{15}H_{10}O_7$. He further shows that *dibromacetyltetrethylquercetin*, $C_{25}H_{26}Br_2O_8$, can be prepared by the interaction of dibromotetrethylquercetin (1 part) and acetic anhydride (10 parts), in presence of zinc chloride (1 part). It dissolves readily in alcohol, crystallises in pale yellow needles, and melts at 154—157°. Dibromoethyleuxanthone, $C_{15}H_{10}Br_2O_4$, which crystallises in yellow needles, and melts at 205—207°, readily yields a *monacetyl* derivative, $C_{17}H_{12}Br_2O_5$. This crystallises in yellow needles or scales, melts at 186—190°, and, on hydrolysis, readily forms the original dibromoethyleuxanthone.

G. T. M.

Phenylcoumalin and "Dicotoïn." By Giacomo Ciamician and Paul Silber (*Ber.*, 1895, **28**, 1549—1558).—Dicotoïn has been shown to be a compound of phenylcoumalin with cotoïn. Phenylcoumalin has the power of combining with many phenols to form crystalline compounds, which, however, become dissociated in solution. *Phenylcoumalin-catechol* forms large, light yellow crystals, melting at 64—66°. *Phenylcoumalin-resorcinol* melts at 110°, and *phenylcoumalin-quinol* at 108°. The resorcinol and catechol compounds crystallise in the monosymmetric system, whilst the quinol compound is asymmetric.

When phenylcoumalin is fused with potash, it yields, among other products, paradiphenylcarboxylic acid, which melts at 224°, although the melting point has been previously stated as 218—219°. It is not impossible that the hydroxyphenylcoumalinic acid, obtained by Hesse by fusing hydroxyphenylcoumalin with potash, may contain a certain amount of this substance. Hydroxyphenylcoumalin is, according to Hesse, a constituent of the pseudodicotoïn which accompanies cotoïn in Coto bark. The authors have carefully examined

the bark, but have been unable to obtain any other substances from it than cotoïn, paracotoïn, and phenylcoumalin. They draw attention to the fact that hydroxyphenylcoumalin and phenylcoumalin possess very similar properties. A. H.

Alantolactone (Helenin). By JULIUS BREDT and WILHELM POSTH (*Annalen*, 1895, **285**, 349—384).—Helenin is the crystalline substance obtained from the root of *Inula Helenium*. Many years ago it was investigated by Gerhardt, Kallen, and others, but the uncertainty of the views regarding its nature has led the authors to submit it to examination, and as its properties are in close agreement with those of the lactone of an unsaturated hydroxy-acid, they propose to call it alantolactone.

Alantolactone, $C_{15}H_{20}O_2$, is obtained on distilling commercial helenin at 192° under a pressure of 10 mm.; it crystallises from alcohol in white needles, and melts at 76°. It is volatile in an atmosphere of steam, and is scarcely soluble in hot water, being readily soluble in organic solvents; the lactone is insoluble in a cold solution of sodium carbonate, which dissolves it when warmed, forming the sodium salt of alantolic acid.

Alantolic acid, $OH{\cdot}C_{14}H_{20}{\cdot}COOH$, is prepared by adding, to an ice-cold solution of the sodium salt, hydrochloric acid in amount insufficient to decompose the whole quantity, in order to avoid formation of the lactone; it melts at 94° (compare Kallen, *Ber.*, 1876, **9**, 155). The *barium* salt crystallises in stellar aggregates, and the crystals which separate from water contain $5H_2O$; the *calcium* salt contains $6H_2O$. The *methylic* salt is very soluble in organic solvents, and melts at 83°; the *ethylic* salt melts at 79—80°. When an aqueous solution of the sodium salt is boiled, separation of the lactone takes place, and this also occurs when a current of carbonic anhydride is led into a boiling solution of the barium salt; on adding a few drops of a dilute, mineral acid to a hot aqueous solution of alantolic acid, immediate separation of the lactone takes place. The amide is obtained from the lactone or from ethylic alantolate by dissolving it in alcoholic ammonia; it melts and decomposes at 197°, and has been already described by Kallen. The *acetyl* derivative of the amide crystallises in needles, and melts with decomposition at 179°. Alantolactone is regenerated when methylic alantolate is heated at 170—180°, methylic alcohol being eliminated; the amide also yields the lactone when heated at 200°, liberation of ammonia taking place.

Alantolactone is an unsaturated compound containing two ethylenic linkings, and the following additive compounds have been prepared. The *monhydrochloride* crystallises in long needles, and melts at 117°, elimination of hydrogen chloride occurring at 150°; the *dihydrochloride* crystallises in needles and leaflets, melts and decomposes at 127—134°, and yields the monhydrochloride when treated with boiling alcohol. The *monhydrobromide* crystallises from alcohol, and melts at 106°; the *dihydrobromide* melts at 117°, hydrogen bromide being eliminated.

Hydroalantolactone, $C_{15}H_{22}O_2$, is obtained by suspending alantolactone in cold water, and allowing it to remain in contact with

sodium amalgam for eight or ten days, and it may be prepared from the mono- and di-hydrochloride also, in the same way; it melts at 123°, and boils at 195° under a pressure of 13 mm. The *hydrochloride* is formed by the action of hydrogen chloride on hydroalantolactone suspended in absolute alcohol; it melts and decomposes at 120°.

The salts of *hydroalantolic acid*, $OH \cdot C_{14}H_{22} \cdot COOH$, are obtained on dissolving the lactone in alkalis. The *barium* salt is anhydrous, and dissolves readily in water, the aqueous solution becoming decomposed at 100—105°, or when submitted to the action of carbonic anhydride. The *silver* salt is somewhat soluble in water, and decomposes after long exposure to light. The *amide* crystallises from alcohol, and melts at 186°, ammonia being liberated.

When alantolactone is heated with phosphoric anhydride at 100° to 120°, liberation of carbonic oxide takes place, and the *hydrocarbons* $C_{13}H_{16}$ and $C_{13}H_{16}$ are formed; both substances are liquid, yield naphthalene when heated, and under a pressure of 10 mm. boil at 132° and 152° respectively, whilst the latter boils at 288° under atmospheric pressure. Distillation of alantolactone from zinc dust gives rise to naphthalene, propylene, and two liquid *hyrdocarbons*, $C_{11}H_{16}$ and $C_{12}H_{18}$, which boil, under a pressure of 10 mm., at 93—94° and 122° respectively, whilst the latter, under atmospheric pressure, boils at 266°, a portion becoming decomposed.

M. O. F.

Phycoerythrin. By H. Molisch (*Chem. Centr.*, 1895, i, 159; from *Apoth. Zeit.*, 1894, 920—921).—Red six-sided prisms of this colouring matter can be observed in the cells of the dead twigs of the alga *Nitophyllum punctatum*. The phycoerythrin dissolves on submerging the alga in water for 24 hours in the dark, and may be precipitated by alcohol. By repeated solution in water and precipitation by alcohol, a pure aqueous solution may be obtained, which yields crystalloids of the colouring matter on spontaneous evaporation; it is insoluble in alcohol, ether, or carbon bisulphide, and is turned green by concentrated potash. It gives the albumin reactions, and is therefore classed as a proteïd. It is bleached by light or dilute potash, and decomposes at 64°; it seems to be identical with the rhodospermin of the various *Bornetia* and *Cordmia*, and with the red colouring matter of the *Nemastoma* and *Wrangelia*.

W. J. P.

Beet Pectin. By K. Andrlik (*Chem. Centr.*, 1895, i, **28**; from *Böhm. Zeit. Zuck. Ind.*, 1894, **19**, 101—113).—The pectin extracted from sliced beet may be precipitated by alcohol; the precipitated pectin contains calcium sulphate which cannot be completely removed, and when fresh is soluble in water, but after drying until its weight becomes constant, it is only partly soluble. The extent to which pectin is precipitated from its solution by alkalis, lime, or magnesia, is dependent on the temperature, but complete precipitation is never effected by these reagents; after precipitating a solution of fresh pectin with lead acetate, the filtered solution is not appreciably active, although the original solutions are dextrorotatory.

W. J. P.

Platosodiammoniodipyridine Compounds. By PETER KLASON (*Ber.*, 1895, **28**, 1489—1492); compare this vol., ii, 400).—According to Jörgensen (*J. pr. Chem.*, 1886, [2], **33**, 501), the same product is obtained by treating ammonioplatosochloramine chloride with pyridine, or pyridineplatosochloropyridine chloride with ammonia. In the same way, the product obtained by treating ammonioplatinous chloride with pyridine is identical with that formed from pyridineplatinous chloride and ammonia, and on treatment with acids yields both ammonioplatinous chloride and pyridineplatinous chloride. This has been explained by Jörgensen by means of structural formulæ, and by Werner on the ground of geometrical isomerism (*Zeit. anorg. Chem.*, **3**, 267). The author finds, however, that when ammonioplatinous chloride is treated with pyridine at a low temperature (5°), a salt which he terms *ammonioplatinosopyridine chloride*, $(NH_3)_2Pt(C_5H_5NCl)_2 + H_2O$, is produced, which has the same composition, but is quite distinct from that obtained by Jörgensen. The latter, which is termed pyridineplatinosammonium chloride, $(C_5H_5N)_2Pt(NH_3Cl)_2 + H_2O$, is obtained when pyridineplatinous chloride is treated with ammonia even at a low temperature. The two salts may be distinguished by their solubility in water, in which the new compound is much more readily soluble than the isomeride, and by their behaviour towards potassium chloroplatinite, chloroplatinic acid, potassium iodide, &c. The new isomeride is completely converted into that previously obtained when it is heated at 100°, or incompletely when its solution in water is boiled. The inverse change appears to take place to some extent when the old salt is heated with acids, as both ammonioplatinous chloride and pyridineplatinous chloride are formed.

The existence of these two isomeric substances shows that the theory of Werner (*Zeit. anorg. Chem.*, **3**, 267), according to which the two should be identical, must receive some modification.

A. H.

Synthesis of Pyridine Derivatives from Coumalin Compounds. By MAX GUTHZEIT (*Annalen*, 1895, **285**, 36—60; compare Abstr., 1894, i, 71).—The action of organic bases on ethylic 6-ethoxycoumalin-3:5-dicarboxylate has been investigated as a sequel to the study of the behaviour of this substance towards dry ammonia (*loc. cit.*). The present paper embodies interesting theoretical considerations with the results of the investigation, which are described in the two following abstracts.

M O. F.

Action of Ethylamine on Ethylic 6-Ethoxycoumalin-3:5-dicarboxylate. By EMIL HAUSSMANN (*Annalen*, 1895, **285**, 61—107).—*Ethylic* 6 : 1 : 2 : 3 : 5-*Ethoxyethylketocarboxydihydropyridinecarboxylate*, $CH\begin{matrix}C(COOEt) : C(OEt)\\ C(COOH) \text{ ----} CO\end{matrix}>NEt$, is obtained by vigorously agitating finely powdered ethylic ethoxycoumalindicarboxylate with an aqueous, 2 per cent. solution of ethylamine for ten minutes; it crystallises in colourless needles and melts at 81°. The compound dissolves with difficulty in light petroleum, but is readily soluble in other organic solvents, and is slightly soluble in hot water, forming an

acid solution. When it is heated at 170°, carbonic anhydride is eliminated, but the quantity set free indicates that a certain amount of the substance loses water at this temperature, forming a stable anhydride. Metallic salts yield a precipitate with a neutral solution of the ammonium salt; the *silver* salt is anhydrous. On heating the compound with fuming hydrochloric acid for six hours at 130—140°, and subsequently at 180°, carbonic anhydride, ethylic chloride, ethylamine hydrochloride are formed. The *diethylic* salt is obtained by the action of ethylic iodide on the silver salt; it crystallises from light petroleum in small, colourless needles, and melts at 56°. The *ethylamine* additive-compound, $C_{13}H_{17}O_6N + 2NH_2Et$, is formed on adding an ethereal 10 per cent. solution of ethylamine to the ethylic salt (m. p. 81°) dissolved in a small quantity of benzene; it is a white, crystalline powder which sinters at 110°, and melts at 158—160°, but when it is suddenly heated to 130° fusion takes place and gas is evolved, the substance solidifying and finally melting at 160°. The additive compound is decomposed by warm water, ethylamine being eliminated, and on treating the liquid with an acid, separation of the ethylic salt takes place.

6 : 1-*Hydroxyethyl*-2-*pyridone*, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CH{:}C(OH)\\CH\text{——}CO\end{matrix}>NEt$, is obtained by heating the ethylic salt (m. p. 81°) with an 11 per cent. solution of potassium hydroxide for three hours on the water-bath; it is a colourless substance which sublimes when heated, and melts at 141°. The aqueous solution colours the skin intense violet, and on adding potassium dichromate to a dilute, acid solution, a deep blue coloration is developed, a green flocculent precipitate being formed when hydrogen peroxide is employed; the latter reagent gives rise to a blue coloration if the solution is alkaline. Silver nitrate and mercuric chloride are reduced by the aqueous solution; a red coloration is developed in the alcoholic solution by ferric chloride, but it gives a reddish-brown precipitate in aqueous solutions. The *hydrochloride* crystallises in brownish leaflets, and decomposes on treatment with water.

Ethylic 6 : 1 : 2 : 3 : 5-*hydroxyethylketocarboxydihydropyridinecarboxylate*, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}C(COOEt){:}C(OH)\\C(COOH)\text{——}CO\end{matrix}>NEt$, is obtained by heating the ethoxy-compound (m.p. 81°) with concentrated sulphuric acid at 100° for $2\frac{1}{2}$ hours; it separates from dilute alcohol in small, colourless crystals and melts at 103°. The compound is also formed when a 5 per cent. solution of alcoholic potash is employed as a hydrolytic agent. Carbonic anhydride is eliminated on heating the substance at 150°, and the residue when dissolved in alcohol develops a deep reddish-violet coloration with ferric chloride, this effect being also produced by the original substance. Solutions of metallic salts, with the exception of mercuric nitrate and silver nitrate, yield a precipitate with a neutral solution of the ammonium salt.

Ethylic 6 : 1 : 2 : 3 : 5-*ethylamidoethylketocarboxydihydropyridinecarboxylate*, $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}C(COOEt){:}C(NHEt)\\C(COOH)\text{——}CO\end{matrix}>NEt$, is formed when the action of an aqueous solution of ethylamine on ethylic ethoxycoumal-

indicarboxylate is allowed to continue during 24 hours; it crystallises in small, colourless needles, and melts at 165°, carbonic anhydride being eliminated above this temperature. The compound is also obtained from the ethylamine additive compound of ethylic ethoxyethylketocarboxydihydropyridinecarboxylate by boiling the solution in benzene. The *ethylamine* salt, $C_{13}H_{15}O_5N_2,NH_2Et$, is prepared by treating the latter compound with an ethereal 10 per cent. solution of ethylamine.

6 : 1 : 2 : 3 : 5-*Ethylaminoethylketodihydropyridinedicarboxylic acid*, $CH\leqslant\begin{matrix}C(COOH):C(NHEt)\\C(COOH)\text{———}CO\end{matrix}\geqslant NEt$, is prepared by allowing ethylic ethoxycoumalindicarboxylate to remain in contact with an aqueous solution of ethylamine for three weeks; it crystallises from alcohol in small leaflets, and if suddenly heated at 180° melts at 191° with evolution of carbonic anhydride. It dissolves in alkalis and alkali carbonates; the alcoholic solution develops a deep-red coloration with ferric chloride. The substance is also formed when the foregoing ethylic salt is hydrolysed with a boiling, aqueous solution of potash (6 per cent.), a small quantity of hydroxyethylpyridine being formed at the same time; the latter compound is not produced, however, when hydrolysis is allowed to proceed at the ordinary temperature during 24 hours. If the ethylic salt (m.p. 165°) is heated with concentrated sulphuric acid for three hours on the water-bath, carbonic anhydride is eliminated and ethylic alcohol is formed, the constitution of the resulting *compound* being represented by one of the formulæ, $CH\leqslant\begin{matrix}C(COOH):C(NHEt)\\CH\text{———}CO\end{matrix}\geqslant NEt$, and

$$CH\leqslant\begin{matrix}CH:C(NHEt)\\C(COOH)\cdot CO\end{matrix}\geqslant NEt.$$

It crystallises from alcohol in colourless leaflets and melts at 207°, after being suddenly heated to 200°, carbonic anhydride being evolved at the higher temperature; an alcoholic solution of the acid gives a deep-red coloration with ferric chloride.

Whilst the foregoing compounds are produced by the action of aqueous elthylamine on ethylic ethoxycoumalindicarboxylate, different results are obtained when water is excluded from the reaction.

Ethylic 1 : 2 : 6 : 3 : 5-*ethyldiketotetrahydropyridinedicarboxylate*, $CH\leqslant\begin{matrix}CH(COOEt)\cdot CO\\C(COOEt)\cdot CO\end{matrix}\geqslant NEt$, is prepared by adding an ethereal $2\frac{1}{2}$ per cent. solution of ethylamine (1 mol.) to ethylic ethoxycoumalindicarboxylate dissolved in the minimum quantity of benzene; it crystallises in colourless needles and melts at 123°. The substance is neutral and the alcoholic solution does not develop colour with ferric chloride. When heated on the water bath with aqueous potash, it yields hydroxyethylpyridone, whilst the action of cold alkali gives rise to a *compound* which melts at 132°. The *ethylamine* additive-compound is a yellow oil having the composition $C_{13}H_{17}O_6N + 2NH_2Et$.

Ethylic 6 : 1 : 2 : 3 : 5-*hydroxyethylketodihydropyridinedicarboxylate*,

$CH\leqslant^{C(COOEt):C(OH)}_{C(COOEt)\text{——}CO}>NEt$, is isomeric with the foregoing compound, and is obtained by heating it to its melting point; it is also formed when a warm ethereal solution of ethylamine acts on ethylic ethoxycoumalindicarboxylate. The substance crystallises from light petroleum in colourless needles and melts at 89·5°; it develops an intense red coloration with ferric chloride, forms salts with alkalis, and does not yield carbonic anhydride under the influence of heat. The *ethylamine* salt is a yellow powder which dissolves readily in water and melts at 181°; the aqueous solution, on treatment with silver nitrate, yields the *silver* salt, $C_{13}H_{16}O_6NAg$, which is not changed by light. The ethyl ether obtained by the action of ethylic iodide on the silver salt melts at 56°; it is identical with the ethyl ether prepared from ethylic ethoxyethylketocarboxydihydropyridinecarboxylate.

When ethylamine and ethylic ethoxycoumalindicarboxylate dissolved in benzene remain together for several days, diethylmalonamide, $CH_2(CONHEt)_2$, is formed (compare Ruhemann and Morrell, Trans., 1891, 43).

The action of dilute aqueous diethylamine on ethylic ethoxycoumalindicarboxylate gives rise to a *compound*,

$$COOEt\cdot CH{:}CH\cdot C(COOEt){:}C(OEt)\cdot NEt_2;$$

it is a basic oil which does not yield a definite hydrochloride. If water is excluded from the reaction, the *compound*,

$$COOEt\cdot C(CONEt_2){:}CH\cdot CH(COOEt)_2,$$

is formed; it is a yellow oil which yields diethylamine when treated with boiling soda.

Aqueous triethylamine is without action on ethylic ethoxycoumalindicarboxylate. M. O. F.

Action of Aniline on Ethylic 6-Ethoxycoumalin-3 : 5-dicarboxylate and on Ethylic Dicarboxyglutaconate. By Georg Band (*Annalen*, 1895, **285**, 108—153).—*Ethylic* 1 : 2 : 6 : 3 : 5-*phenyldiketotetrahydropyridinedicarboxylate*, $CH\leqslant^{CH(COOEt)\cdot CO}_{C(COOEt)\text{—}CO}>NPh$, is prepared by dissolving finely powdered ethylic ethoxycoumalindicarboxylate (10 grams) in a solution of aniline (10 grams) in ether (50 c.c.); it crystallises in pale yellow leaflets, and melts at 147°, becoming solid above this temperature, and melting finally at 197°. The substance dissolves sparingly in ether, alcohol, and light petroleum; it is insoluble in cold water, and is decomposed by boiling water, this effect being also produced by a hot solution of sodium carbonate. The alcoholic solution does not give any coloration with ferric chloride; aniline converts the substance into a compound which crystallises in colourless needles, and melts at 117° (see below).

Ethylic 6 : 1 : 2 : 3 : 5-*hydroxyphenylketodihydropyridinedicarboxylate*, $CH\leqslant^{C(COOEt):C(OH)}_{C(COOEt)\text{—}CO}>NPh$, is isomeric with the foregoing compound, and is obtained by heating it at the melting point or by

treating it with boiling alcohol; the change is also effected by allowing the substance to remain in contact with cold alcohol. It crystallises in slender, white needles, and melts at 197°; it is more soluble in alcohol than the isomeride, and forms a *sodium* salt on treatment with sodium carbonate. The *silver* salt separates on adding silver nitrate to a solution of the sodium salt; it can also be obtained from the *potassium* salt in the same manner. The *ethylic* salt is prepared by the action of ethylic iodide on the silver salt; it crystallises in silky needles and melts at 115°. Ferric chloride produces a deep reddish-violet coloration in the alcoholic solution of the substance, this reaction distinguishing it from the isomeride; the action of aniline also is different, in the cold, there is no action, but boiling aniline converts it into the *dianilide*, $CH\leqslant\begin{matrix}C(CO\cdot NHPh):C(OH)\\C(CO\cdot NHPh)\text{——}CO\end{matrix}\geqslant NPh$; this crystallises from dilute alcohol and melts at 265°.

Reference has already been made to the formation of a compound melting at 117° on treating ethylic phenyldiketotetrahydropyridinedicarboxylate (m. p. 147°) with aniline. This substance is the monanilide of ethylic anilidoethylenedicarboxylate obtained by Ruhemann and Morrell on treating ethylic amidoethylenedicarboxylate with aniline (this vol., i, 20); in preparing it from ethylic dicarboxyglutaconate by the action of aniline, a certain amount of malondianilide is formed, which is also produced on heating the coumalin derivative with aniline. Hydrolysis with alcoholic soda converts it into the *monanilide* of *anilidoethylenedicarboxylic acid*,

$$NHPh\cdot CH:C(CO\cdot NHPh)\cdot COOH,$$

which crystallises in colourless leaflets, and melts and evolves gas at 182·5°.

The *monanilide* of ethylic dicarboxyglutaconate,

$$COOEt\cdot C(CO\cdot NHPh):CH\cdot CH(COOEt)_2,$$

is obtained by adding a solution of aniline in ether to ethylic ethoxycoumalindicarboxylate dissolved in the minimum quantity of benzene, it is a yellow oil, which does not solidify when cooled. This substance is also formed by the action of aniline on ethylic dicarboxyglutaconate; when heated on the water bath, it is converted into ethylic hydroxyphenylketodihydropyridinedicarboxylate (m. p. 197°).

Ethylic diketotetrahydropyridinedicarboxylate, melting at 178—179° (Guthzeit, Abstr., 1894, i, 72), is converted by aniline into the monanilide of ethylic anilidoethylenedicarboxylate (m. p. 117°), malondianilide and the monamide of ethylic malonate being formed at the same time; the same compounds are produced when aniline acts on ethylic ethyldiketotetrahydropyridinedicarboxylate, which melts at 123° (Haussmann, preceding abstract).

An aqueous solution of aniline has the same effect on ethylic ethoxycoumalindicarboxylate as the anhydrous base, converting it into ethylic phenyldiketotetrahydropyridinedicarboxylate (m. p. 147°), and this compound is also formed when a dilute aqueous solution of aniline acetate is employed. M. O. F.

Substituted Amido-derivatives of Aldehydecollidine. By PETER KNUDSEN (*Ber.*, 1895, **28**, 1759—1761).—The aldehydecollidine obtained by the interaction of aldehydeammonia and paraldehyde contains, in addition to methylethylpyridine, small quantities of trimethylpyridine, as already shown by Auerbach (Abstr., 1893, i, 175), who separated the two bases by means of the different solubilities of their mercurochlorides in water. A more convenient method is to convert them into the picrates and to separate these by fractional crystallisation from water, in which trimethylpyridine picrate is readily soluble.

The author has already shown that bromine acts on aldehydecollidine with formation of the substitution product, bromethyl-α-picoline, $C_5NH_3Me{\cdot}CHMeBr$. The bromine atom may be readily displaced by hydroxyl (Abstr., 1893, i, 43), and a similar reaction occurs with primary amido-bases, substituted amido-derivatives of aldehydecollidine being formed. Methylamine converts it into *methylamidocollidine*, $C_6NH_6{\cdot}CHMe{\cdot}NHMe$, which is a colourless liquid, having a penetrating, pyridine-like odour; it is soluble in water, and boils at 223—225°. Its physiological properties strongly resemble those of nicotine. The *hydrochloride*, $C_9N_2H_{14},2HCl$, crystallises in slender needles and melts at 177°, and the *platinochloride*,

$$C_9N_2H_{14},H_2PtCl_6,$$

in flat prisms melting at 243°, whilst the *nitroso-compound* is an inodorous oil. *Anilidocollidine*, $C_6NH_6{\cdot}CHMe{\cdot}NHPh$, is obtained by the action of aniline on bromethyl-α-picoline, and crystallises in reddish-coloured prisms melting at 145—146° (uncorr.); the *hydrochloride* crystallises in slender needles melting at 201—202°, the *platinochloride*, $C_{14}N_2H_{16},H_2PtCl_6$, in prisms which carbonise above 300°, and the *acetyl* compound in snow-white rods melting at 100°.

Attempts were also made to displace the bromine atom in bromethyl-α-picoline by cyanogen, but without success. In presence of water, picolylmethylalkine is formed, and in its absence tarry, brominated condensation products are formed, from which no nitrile could be isolated. H. G. C.

Conversion of Aliphatic Oximes into Pyridine Derivatives. By MAX SCHOLTZ (*Ber.*, 1895, **28**, 1726—1733).—*Cinnamylideneacetone hydroxime*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}NOH$, crystallises in small, pale yellow needles, melting at 153°. The *acetyl derivative* forms lustrous plates and melts at 83°. The oxime is not converted into a pyridine derivative by the action of dehydrating agents, but, when distilled at high temperatures, 2 : 6-*methylphenylpyridine* is obtained; this is a colourless liquid, which quickly turns yellow, volatilises with steam, and boils at 280—281° (corr.). The yield is 25 per cent. of the oxime employed. The *platinochloride*, $(C_{12}H_{11}N)_2,H_2PtCl_6 + H_2O$, crystallises in red needles, and, when dry, melts and decomposes at 200°. The *aurochloride* is deposited in large, golden-yellow needles, melting at 150—151°. The *mercurochloride* crystallises in silky, lustrous, the *picrate* in yellow, needles, and melts at 135°. With chromic acid, the

base yields a dicarboxylic acid, which melts at the same temperature as dipicolinic acid.

When oxidised with the calculated quantity of potassium permanganate, 6 : 2-*phenylpyridinecarboxylic acid* is formed; it crystallises in large, silky, lustrous needles, melts at 109°, and under boiling water, and gives a red coloration with ferrous sulphate; when heated to 190—200°, carbonic anhydride is evolved, and 6-phenylpyridine is formed; this was identified by means of the picrate and platinochloride, and its production proves the constitution of the acid and of the methylphenylpyridine. The *silver salt* of the acid crystallises in small stellate needles; the *hydrochloride* is also crystalline.

2 : 6-*Methylphenylpiperidine*, prepared by the reduction of the pyridine with sodium and alcohol, is a colourless liquid, which boils at 257—259° (corr.). The *hydrochloride* crystallises in colourless needles, the *aurochloride* in sparingly soluble, golden plates, melting at 97°. The *platinochloride*, *picrate*, and *benzoyl derivative* are oily.

Cinnamylideneacetophenone, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}COPh$, prepared from cinnamaldehyde and acetophenone, crystallises in long, golden needles, melting at 102—103°, and gives a cherry-red coloration with concentrated sulphuric acid. The *oxime* crystallises in almost colourless needles, and melts at 131°. When strongly heated, the oxime yields 2 : 6-*diphenylpyridine*, which crystallises in colourless needles, melts at 81°, boils at 396—398° (corr.), yields benzoic acid when oxidised with chromic acid, and is completely decomposed by potassium permanganate. The yield is about 30 per cent. of the oxime employed. This base appears to be identical with the 2 : 6-diphenylpyridine prepared by Doebner and Kuntze by the oxidation of α-phenyl-α-naphthacinchonic acid, but the platinochloride and methiodide differ from those which Paal and Strassner obtained from the diphenylpyridine formed from diphenacylacetic acid and ammonia; the latter compound is therefore probably not the 2 : 6-derivative as they state. The *platinochloride* crystallises with $2H_2O$ in long, orange needles, melting at 195°. The *aurochloride* is deposited in large, yellow needles and melts at 204°. The *picrate* crystallises in dark yellow needles, the *methiodide* in almost colourless prisms, melting at 169° and 194° respectively.

2 : 6-*Diphenylpiperidine*, formed by the reduction of the pyridine, boils at 367—368° (corr.), and becomes viscid when cooled. The *hydrochloride* is crystalline and melts at 298°. The platinochloride and aurochloride could not be prepared; the *picrate* melts at 198°. Cinnamylideneacetone oxime and cinnamyleneacetonphenone oxime, in addition to pyridine derivatives, might also yield compounds containing only 5 atoms in the ring; the former appears to do this, as the lower fraction obtained during the distillation gave the pyrroline reaction, but the substance was only formed in very small quantity.

J. B. T.

Derivatives of Picoline-α-lactic acid. By PETER KNUDSEN (*Ber.*, 1895, **28**, 1762—1773).—A 3-pyridine-α-lactic acid,

$$C_5NH_4{\cdot}CMe(OH){\cdot}COOH,$$

has been obtained by Hardy and Calmels (Abstr., 1886, 724, 815,

900, 1048; 1887, 1057) by the hydrolysis of pilocarpine, but hitherto it has not been obtained synthetically. The homologous picoline-α-lactic acid has been obtained by the author from the 6-picolyl-3-methylalkine formed by the action of water on bromethylmethylpyridine (Abstr., 1893, i, 43). The former substance melts at 36—37°, boils at 252—253° (uncorr.), and is converted by treatment with chromic acid in acetic acid solution into the corresponding *picolyl methyl ketone*, $C_5NH_3Me{\cdot}COMe$; this boils at 232—233°, and forms a *platinochloride*, $(C_8NH_9O)_2H_2PtCl_6$, which crystallises in small plates, and melts and decomposes at 195°. It readily combines with hydrogen cyanide at the ordinary temperature, yielding the *cyanhydrin*, $C_5NH_3Me{\cdot}CMe(OH){\cdot}CN$, which crystallises from benzene in slender needles, melts at 103—104°, and is insoluble in water; this is quantitatively converted, on hydrolysis, into *picoline-α-lactic acid*, $C_5NH_3Me{\cdot}C(OH){\cdot}COOH$, which can be purified by conversion into the barium salt. The acid crystallises from chloroform, on the addition of benzene, in lustrous plates melting at 158—159° (uncorr.). It is very readily soluble in water and alcohol, and when not quite pure can only be obtained as an amorphous, gummy mass. The metallic salts are all amorphous; the *hydrochloride*, $C_9NH_{11}O_3.HCl$, crystallises in large prisms or plates melting at 190—191°; the *hydrobromide*,

$$C_9NH_{11}O_3{\cdot}HBr,$$

in large prisms melting at 219—220°; the *platinochloride* in small prisms very soluble in water and alcohol; and the *aurochloride*, $C_9NH_{11}O_3{\cdot}HAuCl_4$, in felted needles melting at 114°. When treated with phosphorus tribromide in carbon bisulphide solution, it is converted into *picoline-α-bromopropionic acid*, $C_5NH_3Me{\cdot}CMeBr{\cdot}COOH$, which is a very unstable syrup, but yields an *aurobromide*,

$$C_9NH_{10}O_2Br,AuBr_3,$$

crystallising in well developed, dark violet plates, and melting at 156—157°. The salts of the acid very readily pass into the corresponding *picolineacrylic acid*, $C_5NH_3Me{\cdot}C(:CH_2){\cdot}COOH$, with separation of a metallic bromide; for its preparation, the barium salt is best employed, the resulting barium salt being decomposed with the requisite quantity of sulphuric acid. It is thus obtained as a brownish syrup with a strongly acid reaction, whose *aurochloride*,

$$C_9NH_9O_2,HAuCl_4,$$

crystallises in small rods melting at 167—168°.

Hardy and Calmels succeeded in synthesising pilocarpine by heating pyridine-α-lactic acid with trimethylamine in a sealed tube; but in view of the readiness with which the picolyl-lactic acid loses hydrogen bromide, a synthesis of a homologue of pilocarpine is unlikely to be effected in this manner, and, in fact, the products of the action are trimethylamine hydrobromide and picolineacrylic acid. At the ordinary temperature, the action proceeds differently, two basic compounds being obtained, one of which can be distilled over in a current of steam, and is a strongly odorous basic oil, soluble in water, and yields with gold chloride the salt $C_{11}N_2H_{18},2AuCl_3$ melt-

ing at 136—138°; it may also be isolated from the mixture of bases by treating them with baryta water and extracting with ether, the non-volatile portion remaining as a barium salt. The ethereal solution on evaporation yields the base in a pure condition, and if it is then dissolved in hydrochloric acid and gold chloride added, the normal *aurochloride*, $C_{11}N_2H_{16},2HAuCl_4$, separates in plates melting at 159—160°. The non-volatile substance readily loses carbonic anhydride forming the volatile base, and yields an aurochloride, $C_{12}N_2H_{18}O_2(AuCl_3)$, which melts at 141—143° and decomposes at 195—200° with evolution of carbonic anhydride. The constitution of these two compounds is probably represented by the following formulæ:—

$$\overset{(6)}{Me}\cdot C_5NH_3\cdot\overset{(2)}{CH}<\begin{matrix}CH_2\\|\\NMe_2\end{matrix} \quad \text{and} \quad \overset{(6)}{Me}\cdot C_5NH_3\cdot\overset{(2)}{C}<\begin{matrix}CH_2\\|\\NMe_2\\|\\COOH\end{matrix}.$$

Dimethylamine acts on picoline-α-bromopropionic acid in a similar manner, forming a volatile base, $C_{10}N_2H_{16}$, which is probably *dimethylamidocollidine*, $C_5MeNH_3\cdot CMe\cdot NMe_2$.

The difference between the behaviour of the author's picoline-α-bromopropionic acid and Hardy and Calmels' pyridine-α-bromopropionic acid makes it somewhat doubtful whether the two acids are strictly homologous, and the author suggests that possibly Hardy and Calmels' acid is in reality pyridine-β-bromopropionic acid. H. G. C.

1 : 3-Dibromoquinoline. By Adolph Claus and Arnaldo Caroselli (*J. pr. Chem.*, 1895, [2], **51**, 477—490; compare Abstr., 1890, 172).—This dibromoquinoline melts at 101°. The *hydrochloride*, $C_9H_5NBr_2,HCl$, crystallises in thick, colourless laminæ, and melts at 202°; water and alcohol dissociate it. The *platinochloride*,

$$(C_9H_5NBr_2)_2,H_2PtCl_6,$$

forms yellow needles and decomposes at 289°.

4 : 1 : 3-Nitrodibromoquinoline melts at 159° (not 162°, *loc. cit.*), and the corresponding *amido*-derivative at 178—180°. The latter yields a *methiodide* which crystallises in yellow needles and melts at 238°; this fact is of interest as indicating that the entrance of an amido-group into the 4-position confers upon 1 : 3-dibromoquinoline the capacity to combine with methylic iodide, whilst the entrance of this group into the ortho-position hinders such combination; no methiodide has been obtained from 1 : 2 : 4-amidodibromoquinoline. The *hydrochloride* and *platinochloride* of 4 : 1 : 3-amidodibromoquinoline are described; the *zincochloride* decomposes and melts at 325—330°.

1 : 3 : 4-*Tribromoquinoline* is prepared from 4 : 1 : 3-amidodibromoquinoline through the diazo-reaction; it crystallises in colourless, lustrous needles and melts at 159°. Its *hydrochloride* and *platinochloride* are described.

1 : 3 : 3′-*Tribromoquinoline* has been misnamed 1 : 4 : 4′- and 1 : 3 : 4′-tribromoquinoline (Abstr., 1890, 1321; 1891, 82); the latter of these two orientations now stands corrected by the recent observation of Claus and Howitz (Abstr., 1894, i, 617), that 3′-, not 4′-, derivatives

are the products of the Claus-Collischonn method for preparing haloïd quinolines (Abstr., 1887, 60). It melts at 169·5°. This tribromoquinoline is formed when a boiling solution of 1 : 3-dibromoquinoline is brominated with the theoretical proportion of bromine, and this is the sole instance in which bromine can easily be introduced into the 3′-position of a quinoline already substituted in the benzene-ring, without recourse to the Claus-Collischonn method. The best yield of this tribromoquinoline is obtained by brominating 1-quinolinesulphonic acid.

The products of the nitration of 1 : 3 : 3′-tribromoquinoline have already been described (Abstr., 1890, 1321); it is now noted that the supposed nitro-derivative melting at 195° (*loc. cit.*) is not an individual compound, but a mixture of 4 : 1 : 3 : 3′-nitrotribromoquinoline (m. p. 215°) with unchanged tribromoquinoline. When 4 : 1 : 3 : 3′-nitrotribromoquinoline is heated with sulphuric acid, and the liquid thus obtained is diluted and made alkaline with ammonia, a compound which appears to be *hexabromodiquinolyl*, $C_{18}H_6Br_6N_2$, is precipitated; this crystallises in colourless needles and melts at 239°; hot glacial acetic acid and hot chloroform dissolve it, but it is insoluble in alkalis and in hydrochloric acid.

1 : 3 : 4 : 3′-*Tetrabromoquinoline*, previously misnamed 1 : 3 : 4 : 4′- (Abstr., 1894, i, 473), can be sublimed in the form of small, colourless needles; it melts at 205°, and is sparingly soluble in hydrochloric acid and in hot alcohol. A. G. B.

1 : 4-Dibromoquinoline. By Adolph Claus and F. Wolf (*J. pr. Chem.*, 1895, [2], **51**, 490—397).—The nitro-1 : 4-dibromoquinoline previously described (Abstr., 1890, 172), is now shown to be the 3-nitro-derivative. The corresponding amido-derivative melts at 162°, not 165° (*loc. cit.*); no methiodide could be obtained from it; its *platinochloride* is described.

1 : 4 : 3′-*Tribromoquinoline* has been misnamed 1 : 4 : 4′-tribromoquinoline (Abstr., 1891, 83); like the 1 : 3 : 3′-derivative, it yields a diquinolyl-condensation product of high melting point (236°) as well as 3 : 1 : 4 : 3′-nitrotribromoquinoline, when it is nitrated (compare preceding abstract). A. G. B.

1 : 3-Dimethylquinophthalone and 1 : 3-Dimethylquinaldinic acid. By Georg Panajotow (*Ber.*, 1895, **28**, 1511—1513).—1 : 3-*Dimethylquinophthalone*, $C_9NH_4Me_2{\cdot}CH\lessdot^{O{\cdot}CO}_{C{\cdot}C_6H_4}$ [CH = 2′; CO : C = 1 : 2], is prepared by heating dimethylquinaldine with phthalic anhydride and zinc chloride at 140—150°; after purification, it crystallises from glacial acetic acid in yellow needles, melts at 282°, and is insoluble in water and alcohol. The yield is equal to the quinaldine employed. The *sulphonic acid*, $C_{20}H_{14}O_2N{\cdot}SO_3H$, is brownish-yellow and amorphous; it dissolves in water, and dyes silk and wool, directly, of a golden yellow colour. The *nitro-derivative*, $C_{20}H_{14}O_2N{\cdot}NO_2$, is colourless, flocculent, and amorphous. *Dimethylquinaldinic acid*, $C_9NH_4Me_2{\cdot}COOH$ [Me : Me : COOH = 1 : 3 : 2′], obtained when the

phthalone is oxidised by chromic acid, crystallises from alcohol in yellow needles, and gives an amorphous platinochloride. The yield is small. J. B. T.

Anthrapyridine. By A. PHILIPS (*Ber.*, 1895, **28**, 1658—1660).—The anthrapyridines corresponding with the α- and β-anthrapyridinequinones described by the author (Abstr., 1894, i, 554), may be obtained from these by warming them with zinc dust and dilute aqueous ammonia. *β-Anthrapyridine*, $C_{13}H_9N$, is usually obtained in amorphous flocks, but on sublimation forms yellow, nacreous plates, the greater portion of the substance being, however, carbonised. It is sparingly soluble in water, readily in the other common solvents, the solutions having a blue or bluish-green fluorescence, whilst the salts are yellow, and give greenish-yellow solutions with a green fluorescence. The *hydrochloride* crystallises is small, yellow needles, and the *platinochloride* in microscopic prisms. *α-Anthrapyridine* is also usually obtained in amorphous flakes, but sublimes in reddish-yellow needles, a large amount of carbonisation also taking place; it melts at 275°, and is less soluble than the β-compound. The solutions of the salts only show a slight fluorescence. H. G. C.

Synthesis of Dihydroglyoxalines. By GEORGE C. CLAYTON (*Ber.*, 1895, **28**, 1665—1669).—The readiness with which allylbenzamide undergoes condensation with formation of an oxazoline (Kay, Abstr., 1894, i, 77) has led the author to examine the behaviour of the acidyl allylamines towards aromatic amido-compounds; the results show that dihydroglyoxalines may be readily obtained in this manner.

Allylacetamide, $CH_2{:}CH{\cdot}CH_2{\cdot}NHAc$, obtained by heating allylthiocarbimide with acetic acid for 36 hours, under slightly increased pressure, after rectification boils at 215°, and has a sp. gr. = 0·9608 at 15°; it combines with hydrogen chloride to form a hygroscopic *hydrochloride*.

Allylformamide, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}COH$, is obtained in a similar manner from allylthiocarbimide and formic acid, and boils at 109° under 15 mm. pressure; its sp. gr. = 1·0078 at 0°.

2 : 5 : 4-*Dimethylphenyldihydroglyoxaline*, $CHMe<\begin{matrix}NPh{\cdot}CMe\\ CH_2{\cdot}N\end{matrix}$, is obtained by heating allylacetamide and aniline hydrochloride at 180° for 10 hours; the product is treated with dilute hydrochloric acid, which leaves acetamide undissolved, the solution being shaken with ether to remove the last traces of this substance, made alkaline, and again extracted with ether. The dihydroglyoxaline is a colourless oil, which has an ethereal, and at the same time a quinoline-like odour, and yields a hygroscopic *hydrochloride*.

2 : 5 : 4-*Dimethylparatolyldihydroglyoxaline*, obtained in a similar manner from allylacetamide and paratoluidine hydrochloride, is an oily base, which boils at 145° under 15 mm. pressure.

2 : 5 : 4-*Methyldiphenyldihydroglyoxaline*, prepared from aniline hydrochloride and allyl benzamide, is crystalline, melts at 65°, and boils at 192° under 12 mm. pressure. These three bases may also be

obtained by heating allylamine hydrochloride with acetanilide, aceto-paratoluidide, and benzamide respectively.

The mechanism of the action in the formation of the dihydroglyoxalines is explained by the author in the following manner.

$$HCl,NH_2Ph + \underset{\displaystyle NH\cdot CH_2\cdot CH{:}CH_2}{\overset{\displaystyle COMe}{|}} = \underset{\displaystyle CH_2{:}CH\cdot CH_2\cdot \overset{\displaystyle \|}{N}}{\overset{\displaystyle NHPh\cdot \overset{\displaystyle \|}{C}Me}{|}}$$

$$+ HCl + H_2O = \underset{\displaystyle CH_3\cdot CHCl\cdot CH_2\cdot \overset{\displaystyle \|}{N}}{\overset{\displaystyle NHPh\cdot \overset{\displaystyle \|}{C}Me}{|}} + H_2O =$$

$$CHMe\!<\!\underset{\displaystyle CH_2\cdot \overset{\displaystyle \|}{N}}{\overset{\displaystyle NPh\cdot \overset{\displaystyle \|}{C}Me}{|}} + HCl + H_2O.$$

The formation of acetanilide and allylamine is explained by the hydrolysis of the first intermediate compound by the water liberated in the reaction.

$$\underset{\displaystyle CH_2{:}CH\cdot CH_2\cdot \overset{\displaystyle \|}{N}}{\overset{\displaystyle NHPh\cdot \overset{\displaystyle \|}{C}Me}{|}} + HCl + H_2O = NHPh\cdot COMe + CH_2{:}CH\cdot CH_2\cdot NH_2,HCl.$$

The reaction is therefore incomplete and reversible, as shown by the fact already mentioned, that the same bases may be obtained by heating allylamine with the acidylamides. H. G. C.

Action of Chloroform and Alcoholic Potash on Diamines: New Synthesis of Benzoylglyoxaline. By G. Grassi-Cristaldi and G. Lambardi (*Gazzetta*, 1895, **25**, i, 224—230).—A mixture of chloroform and alcoholic potash readily acts on orthophenylenediamine hydrochloride with development of heat; the characteristic odour of an isonitrile is at first apparent, but disappears on keeping the mixture at 50° for an hour. The alcohol and chloroform are now distilled off under reduced pressure, and the product distilled in a current of steam; by extracting the residue with ether, benzoylglyoxaline, melting at 170°, is obtained. Hofmann's reaction thus seems to proceed with orthophenylenediamine in such a way as to yield an intermediate isonitrile of the constitution $NH_2\cdot C_6H_4\cdot N{:}C$, which then changes into the glyoxaline, $C_6H_4\!<\!\overset{-N}{NH}\!>\!CH$.

No pure substance could be isolated on similarly treating metaphenylenediamine, but on treating its para-isomeride with chloroform and alcoholic potash, a very small quantity of a crystalline substance was obtained; this melted at about 160°, and approximated in composition to that of a diisonitrile, $C_6H_4(N{:}C)_2$. W. J. P.

Phthalazine. By Siegmund Gabriel and Franz Müller (*Ber.*, 1895, **28**, 1830—1835; compare Abstr., 1893, i, 732).—Phthalazine is better prepared from 1 : 2-*tetrabromo-xylene*, $C_6H_4(CHBr_2)_2$, which is obtained by allowing the theoretical quantity of bromine to drop slowly into 1 : 2-xylene heated to 140°; it melts at 115—117°. It unites with methylic iodide, forming an additive product, which crystallises in pointed, yellow needles, and melts at 235—240°, and when digested with potash yields *dihydromethylphthalazine*,

$$C_6H_4<\begin{matrix}CH\\CH_2\end{matrix}>N_2Me,$$

and 3-methylphthalazone (Abstr., 1893, i, 346); if silver oxide is employed instead of potash, the phthalazone is alone obtained. Dihydromethylphthalazine is an oil with an odour suggestive of that of isoquinoline; it readily oxidises to the phthalazone; the white *hydrochloride* and yellow *picrate* form needles melting respectively at 140—141° and 93—95°. It yields a *methiodide*, which melts at 153—154°, and, when treated with alkalis, forms a base, the *hydrochloride* of which melts at 159—161°.

Phthalazine ethiodide can be prepared like the corresponding methyl compound; it forms yellow needles, melts at 204—210°, and yields a base, that readily oxidises to ethylphthalazone. The last substance can also be prepared from potassic-phthalazone and ethylic iodide; it melts at 55—58°, or 59—60°, according to the method of preparation. With benzylic chloride, phthalazine yields, moreover, a compound which melts at 97—99°, and with ethylic chloracetate a compound which melts at 155—159°, and forms a yellow picrate, melting at 129—131°. C. F. B.

Pyrazines and Piperazines. By Carl Stoehr (*J. pr. Chem.*, 1895, [2], **51**, 449—476; compare Abstr., 1893, i, 486).—Dimethylpyrazine is obtained in good yield by heating ammonium salts (a mixture of chloride and phosphate) with glycerol, which yields acraldehyde, $2NH_3 + 2C_2H_3{\cdot}COH = C_6H_8N_2 + 2H_2O + H_2$. By introducing acetic aldehyde, dimethylethylpyrazine is formed (compare Storch, Abstr., 1886, 1044). To prepare pyrazine, the dimethyl derivative may be oxidised to pyrazinedicarboxylic acid, which yields the base when heated in glacial acetic acid at 200°.

Pyrazine crystallises in colourless prisms, melts at 47°, and boils at 118° (768·4 mm.) (compare Wolff, Abstr., 1893, i, 373). Its vapour burns with a reddish flame, and an odour of hydrocyanic acid. It usually behaves as a monacid base, but is occasionally diacid. The following salts and derivatives have not yet been described. The *nitrate*, $C_4H_4N_2,HNO_3$; the *sulphate*, $C_4H_4N_2,H_2SO_4$ (m. p. 136—137°); the *zinc chloride* compound, $C_4H_4N_2,ZnCl_2$; the *mercuri-chloride*, $C_4H_4N_2,HgCl_2$ (crystallographical measurements given), decomposes and melts at 273°; the *copper sulphate* compound, $C_4H_4N_2,CuSO_4 + 5H_2O$; the *platinic chloride* compounds, $C_4H_4N_2,H_2PtCl_6$ and $(C_4H_4N_2)_2HCl,PtCl_4$; the methiodide, $C_4H_4N_2,MeI$; the *periodide*, which is a crystalline brownish-red precipitate, obtained by adding a solution of iodine in potassium iodide to one of pyrazine; and the *methochloride*, $C_4H_4N_2,MeCl$, together with its *platinum* salts, $(C_4H_4N_2,MeCl)_2,PtCl_4$, and $C_4H_4N_2,MeCl,PtCl_4$, its *mercuri-chloride* $C_4H_4N_2,MeCl,6HgCl_2$ (m. p. 217—218°), and its *gold* salt.

Methylpyrazine has been already described (Abstr., 1894, i, 384); it behaves as a monacid base, and the salts which it forms with mineral acids are more soluble than those of pyrazine. The *picrate*, $C_5H_6N_2,C_6H_3O_7N_3$, crystallises in short prisms, melts at 133°, and dissolves very sparingly in cold water, but more freely in alcohol. The *mercuric chloride* compound, $C_5H_6N_2,2HgCl_2$, melts and decomposes

at 194—195°, and is very sparingly soluble in cold water. The *silver* compound crystallises in slender, colourless needles. The *aurochloride*, $C_5H_6N_2,HAuCl_4$, melts at 116—117°, and is stable only in hydrochloric acid solution, for when water is added, the *salt*, $C_5H_6N_2,AuCl_3$, separates; this melts at 145—146°. The *methiodide*, $C_5H_6N_2,MeI$, melts at 129—130°; the *methochloride* was crystallised, and its *platinic chloride* compound, $(C_5H_6N_2,MeCl)_2,PtCl_4$, *mercuric chloride* compound, and *gold* salt were prepared.

Pyrazinecarboxylic acid (Abstr., 1893, i, 487) crystallises in anhydrous, colourless prisms; its aqueous solution has a strong acid reaction, and gives a reddish-yellow coloration with ferrous sulphate. It melts and decomposes at 229—230°. The barium salt crystallises with $3\frac{1}{2}H_2O$; the copper salt with $2H_2O$.

Methylpiperazine, $C_5H_{12}N_2$, is prepared by reducing methylpyrazine in alcoholic solution by means of sodium; the liquid is diluted with water, distilled, and the distillate evaporated with hydrochloric acid to obtain the hydrochloride, from which the base is liberated by an alkali. It crystallises in lustrous, white laminæ, boils at 155—155·5° (at 763 mm.), and dissolves freely in water, alcohol, chloroform, and benzene, but less freely in ether. Its aqueous solution is alkaline, and it behaves as a diacid base. The *hydrochloride*, $C_5H_{12}N_2,2HCl$, crystallises from hot alcohol in lustrous, colourless needles, melts at 248—249°, and dissolves in water, yielding an acid solution. The *platinochloride*, $C_5H_{12}N_2,H_2PtCl_6$, *mercurochloride*, and *picrate*,

$$C_5H_{12}N_2,2C_6H_3N_3O_7,$$

are described. The *dinitrosamine*, $C_5H_{10}N_2(NO)_2$, prepared by treating the aqueous solution of the hydrochloride with sodium nitrite and hydrochloric acid, crystallises in brilliant, large, dendritic laminæ, melts at 71°, and dissolves sparingly in water and ether, but more freely in alcohol.

Dibenzoylmethylpiperazine, $C_5H_{10}N_2(COPh)_2$, obtained by shaking the hydrochloride with benzoic chloride and caustic soda in aqueous solution, separates, when water is added to its solution in hot alcohol, in colourless, lustrous, well-formed tables, which are anhydrous, and melt at 147°. If the proportion of water added to the alcoholic solution be considerable, the crystals contain $2H_2O$. A. G. B.

Constitution of *n*-Phenylpyrazolone. By R. v. Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 522—525).—The appearance of a paper by Claisen and Haase (this vol., i, 193) elicits some further remarks from v. Rothenburg concerning the constitution of his 1-phenyl-5-pyrazolone (compare this vol., i, 303). Walker's "phenylmethyloxypyrazole" (Abstr., 1894, i, 476) was described in French and English patent specifications in 1893; since it is derived from diacetylphenylhydrazine by loss of water, its constitution is that of a 2 : 3-phenylmethylpyrazolone. A. G. B.

Pyrazolone Derivatives. By R. Himmelbauer (*J. pr. Chem.*, 1895, [2], **51**, 532).—In reference to Knorr's remarks on the phenol form of 1 : 3-phenylmethyl-5-pyrazolone (this vol., i, 396), the author points out that he has obtained an ethylic carboxylate of this pyrazo

lone by the action of ethylic chlorocarbonate on an alkaline aqueous solution of the pyrazolone. This melts at 28°, and is easily hydrolysed by aqueous ammonia, carbonic anhydride being eliminated and methylphenylpyrazolone produced; this fact, together with the absence of the iron reaction, shows that the carboxethyl is attached to oxygen. By heating monochloracetic acid with methylphenylpyrazolone in alkaline solution, Knorr's methylphenylpyrazolonecarboxylic acid (m. p. 178°) is obtained. A. G. B.

Synthesis of Antipyrine. By R. von Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 572—574).—A reply to Stolz (this vol., i, 394). A. G. B.

Isomerism in the Pyrazole Series. By R. von Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 574—577).—A reply to Knorr (this vol., i, 395). A. G. B.

Chemical Equivalence. By R. von Rothenburg (*J. pr. Chem.*, 1895, [2], **51**, 577—578).—In his recent papers (this vol., i, 395—398), Knorr obviously holds the opinion that the methyl and phenyl groups are chemically equivalent, and sets aside the accepted view that they differ in their influence on a compound. To direct attention to this is, in the author's opinion, sufficient to indicate the value of Knorr's criticisms. A. G. B.

Synthesis of Quinazolines. By Stefan v. Niementowski (*J. pr. Chem.*, 1895, [2], **51**, 564—572).—Excellent yields of quinazoline derivatives are to be obtained by heating anthranilic acid or its homologues with amides of fatty acids, although the yield decreases as the molecular weight of the amide increases. Thus, 4′-hydroxyquinazoline is prepared by heating anthranilic acid (13 grams) with formamide (7—8 grams) in a flask for some three hours at 120—130° and crystallising the product from alcohol; the author finds the melting point of this substance to be 212°. In a similar manner, 4′ : 2-hydroxymethylquinazolone (m. p. 238°) has been synthesised from metamidoparatoluic acid and formamide; 2′ : 4′-methylhydroxyquinazoline from anthranilic acid and acetamide; and 4′ : 2 : 2′-hydroxydimethylquinazoline (m. p. 255°) from metamidoparatoluic acid and acetamide (see Abstr., 1889, 1065).

4′ : 2′-*Hydroxyethylquinazoline*, $C_6H_4<\begin{matrix}N=\!=\!=C\,Et\\ |\\ C(OH):N\end{matrix}$, from anthranilic acid and propionamide, crystallises in slender, white needles, melts at 225°, and dissolves in water and most organic solvents, as well as in acids and alkalis. A little propionanilide is formed at the same time. In all cases where a temperature above 140° is requisite to effect these syntheses, the anthranilic acid or its homologues is partly decomposed, with production of an aromatic base, which reacts with the fatty amide, yielding the corresponding anilide, toluidide, &c.

4′ : 2 : 2′-*Hydroxymethylethylquinazoline*, from metamidoparatoluic acid and propionamide, crystallises in yellow needles and melts at 240°; it dissolves freely in organic solvents, except ether, and in acids and alkalis. *Propionmetatoluidide*, which is formed at the same

time, crystallises in white needles, melts at 81°, and dissolves in organic solvents.

4′ : 2-*Hydroxyisopropylquinazoline*, from anthranilic acid and isobutyramide, crystallises in white, lustrous needles, melts at 224°, and dissolves easily in benzene and alcohol, but sparingly in ether and water. Isobutyranilide (m. p. 104°) is produced at the same time. 4′ : 2 : 2′-*Hydroxymethylisopropylquinazoline* is obtained by substituting metamidoparatoluic acid for anthranilic acid. It crystallises in white needles, melts at 228°, and dissolves in organic solvents, acids, and alkalis. *Isobutyrometatoluidide* is formed at the same time; it crystallises in white needles, melts at 85°, and dissolves easily in alcohol, ether, chloroform, and benzene.

Bischler and Muntendam (this vol., i, 398) have named the compound obtained by the author from orthamidoparatoluamide and acetic anhydride, α-hydroxy-β-methylparatoluometadiazine; this is obviously incorrect, since the compound in question is the 4′ : 2 : 2′-hydroxydimethylquinazoline described above. A. G. B.

Amidoquinoxalinecarboxylic acid. By A. Philips (*Ber.*, 1895, **28**, 1655—1657).—The author has previously shown that quinolinic acid may be converted by a series of reactions into amidopyridinecarboxylic acid (Abstr., 1894, i, 301); he has now further subjected the analogous quinoxalinedicarboxylic acid to the same series of reactions, and finds that these proceed in the same manner, yielding as final product amidoquinoxalinecarboxylic acid. Quinoxalinedicarboxylic acid is readily converted into the anhydride $C_6N_2H_4<\begin{matrix}CO\\CO\end{matrix}>O$ by boiling with acetic anhydride, and crystallises from this liquid in long, lustrous, pale brown needles, which melt and decompose at 251°. When gaseous ammonia is passed into the anhydride suspended in benzene, it is converted into the ammonium salt of the corresponding *amide*, $NH_2\cdot CO\cdot C_6N_2H_4\cdot COONH_4$, which crystallises from warm water in colourless needles, melting and decomposing at 225°. The free acid forms colourless needles, melts and evolves gas at 183°, again becoming solid, and then melts a second time at 255°; on treatment with warm water, it takes up a molecule of water, forming the acid ammonium salt of quinoxalinedicarboxylic acid. To convert the acid into amidoquinoxalinecarboxylic acid, it is dissolved in dilute soda, treated with sodium hypobromite, and the excess of the latter removed by sulphurous acid.

Orthamidoquinoxalinecarboxylic acid, $C_6H_4<\begin{matrix}N:C\cdot NH_2\\N:C\cdot COOH\end{matrix}$, forms pale yellow needles, melts and decomposes at 210°, and is readily soluble in acids and bases, forming salts with both. When heated above its melting point, it gives off gas, yielding a brown basic product, which possibly contains amidoquinoxaline. H. G. C.

A new Indicator—Luteol. By Wilhelm Autenrieth (*Arch. Pharm.*, 1895, **233**, 43—48).—When ethoxydiphenylquinoxaline, $OEt\cdot C_6H_3<\begin{matrix}N:C\cdot Ph\\N:C\cdot Ph\end{matrix}$, prepared by the action of benzile on metaethoxy-

phenylenediamine, is treated with phosphorus pentachloride (1 mol.), the corresponding monochlorinated derivative is obtained. After recrystallisation from alcohol, this *ethoxychlorodiphenylquinoxaline* forms yellowish, glistening needles, which melt at 146—147°. The corresponding *hydroxychlorodiphenylquinoxaline*, $OH\cdot C_6H_3Cl<\begin{matrix}N:CPh\\|\\N:CPh\end{matrix}$, obtained when the ethoxy-derivative is hydrolysed with concentrated hydrochloric acid, crystallises from alcohol in yellowish, woolly needles, which melt at 246° and sublime at a higher temperature. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid, forming a deep red solution. It dissolves also in cold potassium, sodium, and ammonium hydroxides and carbonates, forming intense, yellow solutions, and thus possesses a much more strongly marked acid character than the hydroxydiphenylquinoxaline itself, which is slightly basic. The author recommends the use of this hydroxychlorodiphenylquinoxaline, or *luteol*, as an indicator in acidimetry and alkalimetry, as it is extremely sensitive. The solution is made by dissolving 1 gram of luteol in 300 c.c. of pure alcohol, and 3—8 drops of this solution is used for each titration. It is especially recommended for nitrogen estimations by Kjeldahl's method.

Benzoylluteol, prepared by the Schotten-Baumann method, crystallises in glistening, white plates, melts at 192°, and is insoluble in water, but readily soluble in hot alcohol and in ether.

Acetylluteol obtained by heating luteol with acetic anhydride, crystallises in flat, glistening needles, melts at 185—186°, and is readily hydrolysed by hot sodium hydroxide solution. J. J. S.

Formazyl Compounds. By C. JAGERSPACHER (*Ber.*, 1895, **28**, 1283—1287).—The nitrite of acetylamidrazonehydrazone,

$$N_2HPh{:}CMe\cdot C(N_2HPh)\cdot NH_2,HNO_2,$$

(Abstr., 1894, i, 98), when heated with light petroleum, yields three products. (1) Acetylamidrazonehydrazone, formed simply by loss of nitrous acid. (2) A substance which is isomeric with this hydrazone, and is perhaps a stereoisomeride; it crystallises in white, silky needles melting at 136°, and reacts with acetic acid at 250°, in the same way as the normal hydrazone, phenylamidomethylosotriazole being produced. (3) The third product is phenylazomethylosotriazole, $NPh<\begin{matrix}N:CMe\\|\\N:C\cdot N_2\cdot Ph\end{matrix}$, formed by the elimination of water, ammonia, and nitrogen. When phenylazomethylosotriazole is reduced, it is converted into amidomethylphenylosotriazole, identical with that obtained by the action of acetic acid on acetylamidrazonehydrazone. This substance can readily be diazotised, and yields a *diazoamidopiperidine* compound, which crystallises in yellow needles melting at 77°. When the diazo-solution is boiled, *hydroxymethylphenyltriazole*, $NPh<\begin{matrix}N:C\cdot OH\\|\\N:CMe\end{matrix}$, is produced, which melts at 140—142°, and is soluble in alkalis. *Anilidomethyltriazole carbamide*,

$$NHPh\cdot CO\cdot NH\cdot C_2H_3N_3,$$

forms slender, white needles melting at 240°. The corresponding *thiocarbamide* crystallises in flat, white, vitreous needles, and melts at 195°. *Methylphenyltriazolecarboxylic acid*, $NPh<^{N:CMe}_{N:C\cdot COOH}$, prepared by Sandmeyer's reaction, crystallises in colourless needles melting at 189°. A. H.

Constitution of Tetrazolium Bases. By HANS v. PECHMANN and EDGAR WEDEKIND (*Ber.*, 1895, **28**, 1688—1695).—The preparation of tetrazolium bases by the oxidation of formazyl derivatives, NHPh·N:CR·N:NPh, has been previously described (Abstr., 1894, i, 240; this vol., i, 74); attempts to synthesise similar compounds from tetrazine were unsuccessful, as this substance does not readily form additive compounds with alkyl haloïds. When tetrazolium derivatives are oxidised, the phenyl radicle is not eliminated, even when it contains sulphonic, amido-, or nitro-groups.

Ethylic diparaethoxyphenylformazylformate,

$$OEt\cdot C_6H_4\cdot N_2H:C(COOEt)\cdot N_2\cdot C_6H_4\cdot OEt,$$

is prepared by the interaction of paradiazoethoxybenzene (2 mols.) and ethylic acetoacetate (3·5 mols.) in alkaline solution; it crystallises from alcohol in lustrous, dark red plates or needles with a blue reflex, melts at 127—128°, and dissolves in sulphuric acid with a bluish-green colour. The yield is about 53 per cent. of the ethylic acetoacetate employed.

Diparaethoxyphenyltetrazoliumcarboxylic acid chloride,

$$COOH\cdot C<^{N\cdot N\cdot C_6H_4\cdot OEt}_{N:NCl\cdot C_6H_4\cdot OEt},$$

obtained by treatment of the preceding compound with amylic nitrite and alcoholic hydrochloric acid, crystallises from hydrochloric acid, or from alcohol and ether containing hydrochloric acid, in colourless, lustrous prisms; it becomes yellow when heated, softens, and melts at 194—195°. It is quickly decomposed into the betaïne (see below) by cold water. The yield is 60—70 per cent.

Diparahydroxydiphenyltetrazoliumbetaïne,

$$C<\begin{matrix}N\cdot N(C_6H_4\cdot OH)\\ \\ CO\end{matrix}>\begin{matrix}N:N\cdot C_6H_4\cdot OH,\\ \\ O\end{matrix}$$

is formed by boiling the above chloride with soda, or by heating with hydrobromic acid, but is best prepared by the action of fuming hydrochloric acid at 140—145°; it crystallises with $3\frac{1}{2}H_2O$ in colourless, hexagonal plates, melts and decomposes at 178—179°, and dissolves in alkalis with a reddish-yellow colour. The yield is 50—60 per cent. of the acid employed. When oxidised in dilute nitric acid solution with potassium permanganate, at a temperature not exceeding 25°, it is converted almost quantitatively into tetrazine, the *silver salt* of which crystallises from dilute nitric acid in prismatic needles,

which explode when heated. A direct proof is thus afforded of the constitution of the tetrazolium compounds.

Diparaethoxyphenylformazylformic acid,

$$OEt\cdot C_6H_4\cdot N_2H{:}C(COOH)\cdot N{:}N\cdot C_6H_4\cdot OEt,$$

prepared from the ethylic salt (see above) by heating it with alcohol and soda during four minutes, is deposited from absolute alcohol in almost black plates with a blue reflex, from dilute alcohol in red needles; it melts at 147—148°.

Ethylic diparaethoxyphenyltetrazoliumcarboxylate chloride,

$$COOEt\cdot C\begin{matrix}N\cdot N\cdot C_6H_4\cdot OEt\\ \|\\ N{:}NCl\cdot C_6H_4\cdot OEt\end{matrix}'$$

is obtained from the formazylformate, alcoholic hydrochloric, and nitrous acid at 0°; it is purified with difficulty, crystallises from a mixture of alcohol and ether in colourless prisms, melts at 187°, and is converted into the betaïne (see above) by the action of hydrochloric acid.

Diparaethoxyphenyltetrazoliumbetaïne,

$$C\begin{matrix}N\cdot N(C_6H_4\cdot OEt)\\ \|\\ N{:}N\cdot C_6H_4\cdot OEt,\\ CO\text{———}O\end{matrix}$$

prepared by the action of water or alkali carbonates on the preceding compound, crystallises with $2H_2O$ in well developed, pale orange-yellow, hexagonal plates, melting at 113°.

Diparahydroxyphenylformazylformic acid,

$$OH\cdot C_6H_4\cdot N_2H{:}C(COOH)\cdot N_2\cdot C_6H_4\cdot OH,$$

is obtained by the reduction of the betaïne by means of sodium amalgam in alkaline solution; it crystallises from glacial acetic acid in dark green plates, melts at 186°, and gives an indigo-blue coloration with sulphuric acid.

Ethoxybenzeneazoacetoacetic acid, $COOH\cdot CAc{:}N\cdot NH\cdot C_6H_4\cdot OEt$, is obtained as sodium salt in the preparation of ethylic diparaethoxyphenylformazylformate, from which it is separated by treatment with amylic nitrite and hydrochloric acid; it is less soluble than the latter compound, crystallises from alcohol in yellow prisms, melts at 172—173°, and dissolves in dilute alkalis and alkali carbonates. *Dimeta-* and *dipara-nitrophenylformazyl hydride*, prepared from malonic acid, meta-, and para-nitrodiazobenzene respectively in acetic acid solution, crystallise in brownish-red needles. *Ethylic dimetanitrophenylformazylformate*, from ethylic acetoacetate and metanitrodiazobenzene chloride in alkaline solution, is deposited in small, red needles melting at 217°. *Ethylic dimetanitrophenyltetrazoliumcarboxylate chloride*, prepared by the action of amylic nitrite and hydrochloric acid on the preceding compound, is deposited in slender, colourless crystals melting at 175—176°. *Diparamethoxyphenylformazyl hydride*, formed from malonic acid and paradiazomethoxybenzene acetate, crystallises in red prisms and melts at 88°.

The formation of carbon-nitrogen compounds containing five atoms in the ring is not confined to the formazyl derivatives. Zincke has

obtained a triazolium base from benzeneazo-β-naphthylphenylamine (this vol., i, 238), and the author has previously prepared compounds (ozotetrazones) with six atoms in the ring, but all attempts to obtain closed chains of three and four atoms, $RC\begin{smallmatrix}NR\\|\\NR\end{smallmatrix}$ or $CH\begin{smallmatrix}N-\\|\\NR\end{smallmatrix}>NR$, have been fruitless. J. B. T.

Action of Bromine on Thiocarbimides. By MARTIN FREUND (*Annalen*, 1895, **285**, 154—166).—An introduction to the two following papers. The action of bromine on aromatic and aliphatic thiocarbimides alike results in the formation of a mixture of the sulphide and oxide of the thiocarbimide employed, arising from the decomposition by water of the unstable intermediate products. If water, however, is excluded from the reaction, and the product, suspended in light petroleum, is submitted to the action of hydrogen sulphide, the sulphide alone is obtained, the oxide forming the sole product if water is present from the outset.

Disulphazolidine is the name proposed by the author for the ring composed of an imido-group, two sulphur atoms and two methylene groups, the relative position of the sulphur atoms being indicated by numerals; 2 : 3-disulphazolidine, therefore, has the constitution $\overset{(1)}{NH}\begin{smallmatrix}\overset{(2)}{S}-\overset{(3)}{S}\\|\quad|\\\underset{(5)}{CH_2}\cdot\underset{(4)}{CH_2}\end{smallmatrix}$. Thiuret, obtained by Fromm on oxidising α-phenyldithiobiuret with iodine (Abstr., 1893, i, 575), has the constitution $NH\begin{smallmatrix}C(NPh)\cdot S\\|\\C(NH)-S\end{smallmatrix}$, and is called 2-*phenylimido*-5-*imido*-3 : 4-*disulphazolidine*.

The sulphides dealt with in the following papers are either of this type or derived from 2 : 5-dimethylenetrisulphide, $S\begin{smallmatrix}CH_2\cdot S\\|\\CH_2\cdot S\end{smallmatrix}$. The oxides, on the other hand, are regarded as derivatives of the hypothetical substance 3-thio-2 : 4-biazsulpholid-5-on, $\overset{(1)}{S}\begin{smallmatrix}\overset{(2)}{NH}\cdot\overset{(3)}{C}S\\|\\CO\cdot\underset{(5)}{NH}\end{smallmatrix}\underset{(4)}{}$. M. O. F.

Action of Bromine on Methylthiocarbimide. By MARTIN FREUND and ERNST ASBRAND (*Annalen*, 1895, **285**, 166—183).—3-*Thio*-2 : 4-*dimethylbiazsulpholid*-5-*on*, $S\begin{smallmatrix}NMe\cdot CS\\|\\CO-NMe\end{smallmatrix}$, is obtained in the form of the *tribromo*-derivative, $C_4H_6N_2S_2OBr_3$, on adding a solution of bromine in chloroform to methylthiocarbimide in the same solvent, mixed with half its volume of alcohol. The tribromo-derivative crystallises in orange prisms, and melts at 158°. When exposed to air, or when treated with water, alcohol, acetone, sulphurous acid, or acetic anhydride, it is converted into the *hydrobromide*, $C_4H_6N_2S_2O,HBr$, which crystallises from hot water in greenish-yellow needles, and melts at 227°. From this salt, the base is obtained by treatment with cold alkali; it crystallises in magnificent

six-sided prisms, and melts at 108°. It dissolves sparingly in hot water, and is insoluble in cold, but is soluble in alcohol and ether, and dissolves very readily in chloroform; the base is volatile in an atmosphere of steam, and scarcely undergoes decomposition on distillation. The *hydrochloride* is colourless, and melts at 223°; it becomes dissociated when the aqueous solution is boiled, resembling the hydrobromide in this respect. The *aurochloride* is yellow, and melts at 182°; the *platinochloride* is a reddish-brown varnish, and the *mercurichloride* is a white, crystalline substance which melts at 216°. When reduced with ammonium sulphide in alcoholic solution, the base yields dimethylthiocarbamide, and a mixture of this substance with monomethylthiocarbamide is obtained on treating it with alcoholic ammonia; dimethylthiocarbamide melts at 61° (compare Hecht, Abstr., 1890, 477). The base is indifferent towards hydrochloric acid at 100°, but methylamine hydrochloride is obtained on heating it with the reagent for three hours at 200°. *Triphenylthiobiuret* is produced on boiling the solution of the base in aniline until the liquid acquires a brownish-black colour; hydrogen sulphide is liberated and sulphur is formed, whilst triphenylthiobiuret, which melts at 234°, crystallises out on allowing the solution to cool.

The *methylamine* salt of methylthiocarbamic acid,

$$HS{\cdot}CO{\cdot}NHMe,NH_2Me,$$

is prepared by leading a current of carbon oxysulphide into an alcoholic solution of methylamine; it melts at 120—121°, and forms colourless crystals, which become yellow and decompose in air. The action of oxidising agents gives rise to methylamine and sulphur.

1-*Methyl*-2-*methylimido*-5-*thio*-3 : 4-*disulphazolidine*,

$$NMe\begin{<}C(NMe){\cdot}S \\ CS\text{---}S\end{>}$$

results from the action of bromine on methylthiocarbimide and subsequent treatment of the product with hydrogen sulphide; it is also obtained by the action of bromine on the methylamine salt of methyldithiocarbamic acid dissolved in aqueous alcohol. It crystallises from alcohol in nacreous leaflets, and melts at 86°. The *tribromo*-derivative, $C_4H_6N_2S_3Br_3$, is an orange powder which yields the *hydrobromide* $C_4H_6N_2S_3,HBr$, when heated; this salt forms yellow transparent crystals, and melts at 248°. The *hydrochloride* melts at 227°, and the *nitrate* melts and decomposes at 130—132; the *sulphate* crystallises in long, six-sided prisms, and melts at 221°. The tribromo-derivative may be obtained by the action of bromine on *dimethylthiocarbamine bisulphide*, NHMe·CS·S·S·SC·NHMe, which is prepared by adding bromine water to an aqueous, 33 per cent. solution of methylamine mixed with carbon bisulphide and alcohol, and agitating the liquid with ether; on evaporating the ether, a crystalline substance is obtained which melts and decomposes at 109°, and yields hydrogen sulphide and methylthiocarbimide when treated with boiling alcohol or water.

2 : 5-*Dimethylimidodimethylenetrisulphide*, $S\begin{<}C(NMe){\cdot}S \\ C(NMe){\cdot}S\end{>}$, is isomeric

with 1-methyl-2-methylimido-5-thio-3 : 4-disulphazolidine, from which it is obtained by heating it at the melting point, and also by treating the alcoholic solution with potash, soda, ammonia, sodium ethoxide, or aniline. Treatment with alcoholic ammonia affords the most convenient method of preparation, and the substance is obtained in greenish, six-sided prisms which melt at 120°. The *bromo*-derivative melts at 127—128°; the hydrobromide (m. p. 248°) of the original base is obtained by treating the isomeride with boiling hydrobromic acid.

When 1-methyl-2-methylimido-5-thio-3 : 4-disulphazolidine is reduced in alcoholic solution with zinc dust and sulphuric acid, dimethylthiocarbamide is produced, but this substance has not been obtained by treating the isomeride with an acid or an alkaline reducing agent; when, however, it is heated with alcoholic ammonia for two hours at 100°, monomethylthiocarbamide is formed. On oxidising the base (m. p. 86°) with nitric acid (sp. gr. 1·16) methylamine nitrate is produced. Dimethylcarbamide is not present in the mixture of compounds obtained by treating the isomeride (m. p. 120°) in alcoholic solution with mercuric oxide. M. O. F.

Action of Bromine on Ethylthiocarbimide and Phenylthiocarbimide. By MARTIN FREUND and GREGOR BACHRACH (*Annalen*, 1895, **285**, 184—203).—3 - *Thio* - 2 : 4 - *diethylbiazsulpholid* - 5 - *on*, $S<\begin{matrix}NEt\cdot CS\\ |\\ CO—NEt\end{matrix}$, resembles the dimethyl derivative (preceding abstract) in the method of its preparation; it melts at 45°, and crystallises in monoclinic plates, taking the form of long needles, when separation from the solvent is rapid. It is volatile in an atmosphere of steam, and is indifferent towards boiling water; the base boils without undergoing change. The *tribromo*-derivative crystallises in orange-red, six-sided prisms, and melts, undergoing decomposition at 180—181°; the *hydrobromide* forms slender, silky needles, and melts at 202°. The *hydriodide* and *hydrochloride* melt at 145° and 185° respectively; the *mercurichloride*, $(C_6H_{10}N_2SO,HCl)_2,3HgCl_2$, crystallises in feathery aggregates of needles which melt at 131—132°, and the *aurochloride* melts at 167·5°. Reduction of the base gives rise to diethylthiocarbamide, and triphenylthiobiuret (*loc. cit.*) is obtained by the action of aniline.

1-*Ethyl*-2-*ethylimido*-5-*thio*-3 : 4-*disulphazolidine*, $NEt<\begin{matrix}C(NEt)\cdot S\\ |\\ CS——S\end{matrix}$, is obtained by adding a solution of bromine in light petroleum to ethylthiocarbimide in the same medium; the crystals which separate consist of the *hydrobromide* melting at 207°, and the base is obtained by decomposing this salt with soda after crystallisation from water. It separates from methylic alcohol in long, yellow needles, and melts at 29·5°; it boils without undergoing decomposition. The *hydrochloride* melts at 175°, the *nitrate* at 70—72°, and the *sulphate* at 176—178°. The base is also obtained from *diethylthiocarbamine bisulphide*, NHEt·CS·S·S·SC·NHEt, which is prepared from the ethylamine salt of ethyldithiocarbamic acid by the action

of bromine water; the bisulphide melts at 78—79°, and on treating the chloroform solution with bromine in the same medium, separation of ethylmethylimidothiodisulphazolidine takes place.

Alcoholic ammonia converts the base into ethylthiocarbamide, and diethylthiocarbamide is obtained on treating it with alcoholic ammonium sulphide; when heated with hydrobromic acid at 150—160°, sulphur, hydrogen sulphide, and ethylamine are produced. Attempts to obtain an isomeride analogous to dimethylimidodimethylenetrisulphide (*loc. cit.*) were unsuccessful.

3-*Thiodiphenyl*-2 : 4-*biazsulpholid*-5-*on*, $S<\begin{matrix}NPh\cdot CS\\ CO—NPh\end{matrix}$, is obtained in the form of the *hydrobromide* (m. p. 203°) by adding a chloroform solution of bromine to phenylthiocarbimide dissolved in chloroform mixed with alcohol; the base has been already described by Helmers (Abstr., 1887, 581). The *hydrochloride* melts at 175°. Diphenylthiocarbamide is produced on reducing the base with alcoholic ammonium sulphide, and the action of boiling aniline results in the formation of triphenylthiobiuret.

1-*Phenyl*-2-*phenylimido*-5-*thio*-3 : 4-*disulphazolidine*,

$$NPh<\begin{matrix}C(NPh)\cdot S\\ CS\ \ —S\end{matrix}.$$

has been already described (Abstr., 1892, 984), and appears to be identical with phenyldithiocarbamic thioanhydride (Losanitsch, Abstr., 1892, 55), because it can be obtained by treating ammonium phenyldithiocarbamate with a solution of bromine in light petroleum. It melts at 154—156°, and is not basic in character; alcoholic potash converts it into phenylthiourethane (m. p. 71—72°), and diphenylthiocarbamide is formed on reducing it with alcoholic ammonium sulphide. All attempts to prepare it from diphenylthiocarbamine disulphide have been unsuccessful. M. O. F.

The Quinine Alkaloïds. By Oswald Hesse (*Ber.*, 1895, **28**, 1298—1302).—When quinine hydrate, in alcoholic solution, is treated with methylic iodide, quinine methiodide, $C_{20}H_{24}N_2O_2MeI + 2H_2O$, is formed. The corresponding *sulphate* has the composition

$$(C_{20}H_{24}N_2O_2Me)_2SO_4 + 6H_2O,$$

whilst the *hydroxide* is a strongly basic, white mass. Boiling aqueous potash converts the methiodide into a substance which has been described by Claus and Mallman (*Ber.*, **14**, 76) as methylquinine, but appears to be methylquinicine. The author proposes to confirm this view by preparing the methyl derivative of quinicine and comparing the two. A. H.

Reduction of Cinchonine. By Fr. Konek Edler v. Norwall (*Monatsh.*, 1895, **16**, 321—332).—On reduction in absolute alcoholic solution with sodium, cinchonine yields a dark yellow oil, soluble in ether, and drying to a gummy mass. This product is strongly basic, and gives a non-crystalline *sulphate* and a brownish-yellow, flocculent *platinochloride*, which appears to be a mixture of two (or more) com-

pounds, $X_2H_2PtCl_6$ and $X_2H_2PtCl_6$, where X represents cinchonine or hydrocinchonine. From the gummy reduction products, amorphous substances have also been isolated; these soften at 40—50°, melt at 60—80°, and appear to have the composition of dihydrocinchonine.

On reduction in acetic acid solution with sodium, an oil is obtained, which is soluble in ether. It dissolves in hydrochloric acid, and, when fractionally precipitated with ammonia, yields yellow, amorphous masses of dihydrocinchonine, $C_{19}H_{24}N_2O$, and from this the dihydriodide, $C_{19}H_{24}N_2O,2HI$, was prepared in the form of reddish-yellow flocks.

When dissolved in concentrated hydrochloric acid solution and treated with metallic tin, cinchonine yields a molecular compound of cinchonine and cinchonine hydrochloride, $C_{19}H_{22}N_2O,C_{19}H_{23}N_2OCl$. This crystallises from a mixture of benzene and alcohol in needles, melts at 228°, and, on trituration with hydrochloric acid, forms a sparingly soluble hydrochloride, $C_{19}H_{23}ClN_2O,2HCl$, from which König's hydrochlorocinchonine (*Ber.*, **20**, 2519) may be separated on the addition of soda. Zoin's chlorocinchonide (Hesse's hydrochloroäpocinchonine), obtained on heating cinchonine with hydrochloric acid at 140—150°, appears to be identical with the latter. G. T. M.

Inosic acid. By Franz Haiser (*Monatsh.*, 1895, **16**, 190—207).—The author shows that the inosic acid obtained by Liebig from meat extract contains phosphorus as one of its constituents. The acid was obtained from meat extract as the silver salt, and this was converted into the barium salt by precipitating the silver with hydrogen sulphide, and then treating with barium carbonate.

The *barium salt*, $C_{10}H_{11}BaN_4PO_8 + 7\frac{1}{2}H_2O$, crystallises in four-sided plates, which, when dry, have the appearance of polished silver. It loses $6\frac{1}{2}H_2O$ at 100—105°, and the remaining H_2O when heated at 100° under diminished pressure.

An insoluble *basic barium salt* is formed when barium hydroxide is added to the aqueous solution of any salt of inosic acid. When dried at 100°, it has the composition $Ba_3(C_{10}H_9N_4PO_8)_2 + 2H_2O$.

The *calcium salt*, $C_{10}H_{11}CaN_4PO_8 + 6\frac{1}{2}H_2O$, forms colourless, transparent, monoclinic crystals, which are readily soluble in hot water.

The *potassium* and *ammonium* salts are very hygroscopic, and can be obtained in a crystalline form only with great difficulty. *The acid* itself, $C_{10}H_{13}N_4PO_8$, is decomposed when heated for some time in aqueous solution. The resulting products are sarkine, and two substances which could not be obtained quite pure, but are probably trihydroxyvaleric acid and trihydroxyvalerophosphoric acid. A similar decomposition occurs when inosic acid is treated with tin and hydrochloric acid. J. J. S.

Organic Chemistry.

Double Salts of Silver and of Mercury containing Cyanogen. By F. W. Schmidt (*Zeit. anorg. Chem.*, 1895, **9**, 418—433).—Long, well-developed crystals are obtained when ammoniacal mercuric cyanide solution is allowed to remain for a considerable time at low temperatures. The compound is unstable, and at the ordinary temperature dissolves in the mother liquor, crystals of ammoniomercuric cyanide, $Hg(CN)_2,NH_3$, being formed; this has been previously prepared in a different manner by Varet. Silver nitrate solution, when mixed with saturated mercuric cyanide solution, gives a sparingly soluble, crystalline, additive compound,

$$Hg(CN)_2,AgNO_3,2H_2O,$$

which explodes when heated, but with more dilute solutions, or in presence of nitric acid, no precipitate is formed. The compounds $CN\cdot HgNO_3,OH\cdot HgNO_3,10AgCN$ and $OH\cdot HgNO_3,20AgCN,5Ag_2O + 7H_2O$ are formed by mixing a cold saturated ammoniacal mercuric cyanide solution with 5 and 2 parts respectively of aqueous silver nitrate (10 per cent.); both are colourless, amorphous, pulverulent, and sparingly soluble, but do not explode when heated. When the above solutions are mixed in the proportion of 1 : 0·3—1·2 of silver nitrate, pure silver cyanide is precipitated; the further addition of silver nitrate causes a steady decrease of silver in the precipitates. The compound $OH\cdot HgNO_3,AgCN,2H_2O$ is obtained in crystals when ammoniacal mercuric cyanide solution (25 c.c.) is mixed with water (225 c.c.) acidified with nitric acid, and silver nitrate (100 c.c.) added; it explodes violently when heated. By the interaction of silver nitrate (7·5 grams), water (7·5 grams), concentrated ammonia (30 c c.), and ammoniacal mercuric cyanide (20 c.c.), a compound, $2OH\cdot HgNO_3,2AgCN,4Ag_2O,3NH_4CN$, is formed, which crystallises in plates, and explodes slightly when heated. The compound $4OH\cdot HgCN,3AgCN,2Ag_2O,NH_4\cdot CN + \frac{1}{2}H_2O$ is formed like the preceding salt, if the silver nitrate is first precipitated with soda and the oxide dissolved in concentrated ammonia (50 c.c.). It is yellow, pulverulent, and somewhat unstable, but does not explode when heated. In all the above experiments, a cold, saturated solution of ammoniacal mercuric cyanide, and a 10 per cent. solution of silver nitrate, were employed. For the analysis of the above compounds, the mercury was determined as sulphide, the silver precipitated as chloride and cyanide, converted into sulphide by means of ammonia and ammonium sulphide, and this into metal by cautious roasting.

Potassium triiodide and silver nitrate in aqueous or alcoholic solution give a dark brown precipitate, which probably consists of *silver triiodide*, AgI_3; it is unstable, and readily dissolves in excess of potassium triiodide. Iodine added to highly dilute ammoniacal silver nitrate

solution gives a white, flocculent precipitate, which becomes yellow when dry, and is possibly silver hypoiodite. J. B. T.

Bimolecular Nitriles and their Derivatives. By ERNST V. MEYER (*J. pr. Chem.*, 1895, [2], **52**, 81—117; compare Abstr., 1888, 802; 1889, 113, 114, 683, 684; 1893, i, 314).—On one occasion, when benzene was used instead of ether as a solvent in the preparation of diacetonitrile, the product was found to melt at 74—76°, but after it had been kept at 80° for some time the melting point fell to that of diacetonitrile (52°). This *labile* or *α-diacetonitrile* has been heretofore overlooked, because the product of the action of sodium on acetonitrile has always been crystallised from boiling benzene, a process which converts the labile into the *stable* or *β-diacetonitrile*; α-diacetonitrile melts at 79—84°, and is only about one-seventh as soluble in benzene as the stable form is, so that it remains undissolved when a mixture of the α and β forms is treated with benzene at 35°. In the following experiments, β-diacetonitrile was used.

Chlorodiacetonitrile, $NCl:CMe\cdot CH_2\cdot CN$ (?), is obtained when diacetonitrile is treated with chloride of lime and the product extracted with ether; it crystallises in white needles, and melts at 120°. The corresponding *bromo-derivative* is obtained as a white precipitate when diacetonitrile is agitated with excess of bromine dissolved in potash; it crystallises in colourless needles and melts at 123°. The halogen cannot be removed from either compound by the ordinary reagents.

By heating diacetonitrile with ethylic chlorocarbonate at 100° and extracting the product with ether, a *compound*, $C_{10}H_9N_3O_3$, is dissolved, and a white salt is left. The former crystallises in white laminæ and melts at 84°. The latter contains chlorine, and when heated with dilute potash yields ammonia and a white residue consisting of Holtzwart's base, $C_8H_9N_3$ (Abstr., 1889, 683); this base is very sparingly soluble in water, ether, and benzene, but more freely in alcohol; its *platinochloride*, $(C_8H_9N_3)_2,H_2PtCl_6$, crystallises in sparingly soluble, thin, bright yellow prisms. With acetic anhydride, the base yields a *monacetyl derivative*, $C_8H_8N_3Ac$, which melts at 250°. The base is easily formed from diacetonitrile when this is placed under conditions favourable for the separation of ammonia without access of water, such, for instance, as when it is heated in boiling ethylenic bromide. An *isomeride*, melting at 157°, is obtained when diacetonitrile is treated with carbonyl chloride and the chlorinated product is suspended in water made feebly alkaline with ammonia; when heated with potash, it is converted into Holtzwart's base (m. p. 222°). By treatment with nitrous acid, the isomeric base yields a compound, $C_8H_8N_2O$, similar in composition to that which Holtzwart obtained by heating diacetonitrile with water (*loc. cit*); but it crystallises in small needles, decomposes above 260°, and dissolves to the extent of 0·09 gram in 100 c.c. of alcohol (at 16°), and of 0·042 gram in 100 c.c. of water (at 16°), whilst Holtzwart's compound crystallises in long, lustrous needles, blackens at 230°, and dissolves to the extent of 0·54 gram in 100 c.c. of alcohol (at 16°), and of 0·05 gram in 100 c.c. of water (at 16°). Neither compound combines

with hydroxylamine or phenylhydrazine. The author discusses the constitution of the above substance, but arrives at no conclusion.

The *hydrochloride*, $C_4H_6N_2,HCl$, was obtained as an amorphous, white precipitate on passing hydrogen chloride into a benzene solution of diacetonitrile. With carbanil in a benzene solution, both α- and β-diacetonitrile yield three *compounds:* (1) needles, $C_{11}H_{11}N_3O$, which melt at about 121—122°; (2) laminæ, which melt at about 150° and are also obtained when (1) is dissolved in hydrochloric acid and reprecipitated by an alkali; (3) a crystalline powder which melts at 229°; all three have the same percentage composition.

Diacetonitrile reacts with cyanamide in warm water, with separation of ammonia and formation of a *condensation product*, $C_9H_{10}N_4O$, which crystallises in needles and melts and decomposes at about 145°; when heated with water, it yields the compound $C_8H_8N_2O$.

With diazobenzene chloride, diacetonitrile yields the *phenylhydrazone*, $NH{:}CMe{\cdot}C(N_2HPh){\cdot}CN$, which readily passes into *cyanacetonephenylhydrazone*, $COMe{\cdot}C(N_2HPh){\cdot}CN$; the latter crystallises in yellow, silky needles, and melts at 166—167°. The two compounds combine to form an additive product, $C_{20}H_{19}N_7O$, which crystallises in yellow needles and melts at 165°. The *osazone*,

$$N_2HPh{:}CMe{\cdot}C(N_2HPh){\cdot}CN,$$

was prepared; it melts at 162—170°. Methylisoxazolenimide (Abstr., 1893, 314) and diazobenzene chloride yield the corresponding *phenylhydrazone*, $N\begin{array}{l}<\!\!\!

A *condensation product*, $C_{15}H_{13}N_3$, is obtained on adding concentrated hydrochloric acid to benzaldehyde ($1\frac{1}{2}$ mols.) and diacetonitrile (1 mol.) dissolved in glacial acetic acid; it crystallises in white needles, melts at 205—206°, and dissolves sparingly in ether and benzene, but not in water. If the action takes place in alcoholic solution in presence of sodium ethoxide, the product melts at 201—202°, but is converted into the above compound by dilute sulphuric acid.

Dipropionitrile (Abstr., 1889, 114, 841) is a far less active compound than diacetonitrile, and enters into reaction with diazobenzene chloride alone of the reagents mentioned above. The *compound*, $C_{13}H_{14}N_4$, thus formed, crystallises in microscopic, yellow prisms, and melts at 151°.

Acetopropionyldinitrile (*imidoacetylpropionitrile*),

$$NH{:}CMe{\cdot}CHMe{\cdot}CN,$$

prepared from a mixture of methylic and ethylic cyanide in the manner adopted for diacetonitrile, forms crystals, which melt at 113°. Its *benzoyl* derivative, $C_8H_7BzN_2$, crystallises in white needles, and melts at 98—100°.

Benzacetodinitrile, $NH{:}CPh{\cdot}CH_2{\cdot}CN$, combines with carbanil to form an *additive compound*, which crystallises in needles, melts at about 192°, and is not soluble either in acids or in alkalis. By saturating an alcoholic solution of benzacetodinitrile with hydrogen chloride, a *compound*, $C_{18}H_{12}N_2O$, analogous to that formed by heating diacetonitrile with water, is obtained; this crystallises in long, white needles, and melts at 144°.

Cyanacetophenonephenylhydrazone, $COPh{\cdot}C(N_2HPh){\cdot}CN$, is the product of the reaction between benzacetodinitrile and diazobenzene chloride; it crystallises in yellow needles, melts at 135°, dissolves in ammonia, and yields a *silver derivative*.

With benzaldehyde, benzacetodinitrile yields *benzylidenebenzacetodinitrile*, $\begin{matrix} PhCN \\ | \\ CN{\cdot}CH \end{matrix}{>}CHPh$, which crystallises in rhombic laminæ, and melts at about 260°; it is insoluble in water, and only sparingly soluble in ether and in alcohol.

By the action of nitrous acid on benzacetodinitrile, a *nitrite*, crystallising in needles and melting at 151°, is formed; this loses nitrous acid when treated with hydrochloric acid, yielding *isonitrosocyanacetophenone*, $COPh{\cdot}C(NOH){\cdot}CN$, which forms stellate groups of crystals, and melts at 122°; its *silver* compound was prepared.

Benzopropiodinitrile (imidobenzoylethyl cyanide (Abstr., 1889, 577), yields the *compound*, $C_{10}H_{10}N_2O$, when treated with hydroxylamine; the new substance crystallises in needles, and melts at 92°.

Paratoluacetodinitrile, $NH{:}C(C_6H_4Me){\cdot}CH_2{\cdot}CN$, from methylic cyanide and paratolylic cyanide, crystallises in broad prisms, melts at 108°, and dissolves sparingly in hot water, but freely in ether and benzene. When heated with dilute hydrochloric acid, it is converted into *cyanomethyl paratolyl ketone*, $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}CN$, which crystallises in slender prisms, and melts at 104—105°; the corresponding *oxime* melts at 150—151°. With phenylhydrazine, paratoluaceto-

dinitrile yields laminæ, which melt at 169°, and are too stable to be a phenylhydrazone. *Bromoparatoluacetodinitrile* melts at 164°, and *chloroparatoluacetodinitrile* at 149°. The *benzoyl* derivative of paratoluacetodinitrile melts at 179°, and the *benzylidene* derivative (see above) melts and decomposes at 215°. *Cyanomethyltolylketone phenylhydrazone*, from diazobenzene chloride and paratoluacetodinitrile, melts at 152—153°.

Paratolupropiodinitrile, $NH{:}C(C_6H_4Me)\cdot CHMe\cdot CN$, from paratolylic cyanide and ethylic cyanide, melts at 98—99°; with hydroxylamine it yields, not the appropriate ketoxime (see above), but the isomeric *isoxazolonimide*, $C_{11}H_{12}N_2O$, which crystallises in white prisms, and melts at 134°.

Diphenacetonitrile, $NH{:}C(CH_2Ph)\cdot CHPh\cdot CN$, from benzylic cyanide, is an oil which was identified by the fact that it yielded the same *oxime* (m. p. 107°) as that obtained from *α-cyanophenylmethyl benzyl ketone*, $CH_2Ph\cdot CO\cdot CHPh\cdot CN$; this ketone is prepared by the condensation of ethylic phenylacetate and benzylic cyanide in the presence of sodium ethoxide; it melts at 85—86°, and is converted by gaseous ammonia at 170° into diphenacetonitrile.

Benzophenacetodinitrile, $NH{:}CPh\cdot CHPh\cdot CN$, prepared by the action of gaseous ammonia at 170° on the corresponding ketone (see below), crystallises in laminæ and melts at 146°. *α-Cyanodeoxybenzoïn*, $COPh\cdot CHPh\cdot CN$, prepared by the condensation of ethylic benzoate with benzylic cyanide in presence of sodium ethoxide, melts at 87—90°. A. G. B.

Ethenylic Trisulphide. By P. Candiani (*Gazzetta*, 1895, **25**, i, 81—88).—Ethenylic trisulphide is conveniently prepared by the action of bromine vapour on thioacetic acid in a closed tube at ordinary temperatures; the action is an indirect one, the trisulphide being produced by the agency of the hydrogen bromide which is evolved, for on sealing up thioacetic acid in a tube with an arrangement by which water is caused to act on phosphorus bromide, thus liberating hydrogen bromide under pressure, ethenylic trisulphide is obtained. Cryoscopic determinations in benzene solutions show that the substance has the molecular formula $C_8H_{12}S_6$. For 9·9—11·5 per cent. benzene solutions at 15·9°, the molecular refractions are 137·34 and 77·66, and the atomic refractions of sulphur are 13·58 and 7·53 for the α-hydrogen ray, calculating by the empirical and theoretical formulæ respectively. These values of the atomic refractions approximate closely to those deduced from the refraction constants of ethylic sulphide.

Bromine acts on an ethereal solution of thioacetic acid, yielding a dense, oily substance, which fumes in the air and slowly loses hydrogen bromide during distillation under reduced pressure; it seems to have the composition $C_6H_{10}Br_2SO_2$. W. J. P.

Optically Active Halogen Derivatives. By J. Achille Le Bel (*Ber.*, 1895, **28**, 1923—1924).—The author points out that Walden, in his recent paper having the above title (this vol., i, 450), makes no mention of a previous paper of the author's (Abstr., 1894, ii, 77), in

which the same question was discussed and a number of the same active halogen derivatives described. Thus the author also obtained the active methylic salt of sarcolactic acid, and converted it into the acetin and butyrin, which are lævo-rotatory, whilst Walden's chlorhydrin and bromhydrin are dextro-rotatory, the relation of these compounds being the same as with the corresponding derivatives of secondary amylic alcohol. On the other hand, the active monochlorhydrin of propylene glycol, $CH_3 \cdot CH(OH) \cdot CH_2Cl$, behaves in a totally different manner, as when the hydroxyl is displaced by chlorine the sign of rotation remains unchanged, but changes when hydroxyl is displaced by the acetoxy-, chloracetoxy-, or butyroxy-groups. It is evident, therefore, that halogen derivatives form an exception to Guye's hypothesis. H. G. C.

The Multirotation of Dextrose. By A. Levy (*Zeit. physikal. Chem.*, 1895, **17**, 301—324).—The retrogression of the multirotation of a solution of dextrose is accelerated by the addition of small quantities of acids or strong bases, and the author conducted a series of experiments to determine the comparative effects, in this respect, of various compounds at various concentrations. In these determinations, the half shadow apparatus of Schmidt and Haensch was employed, the tube being 80 mm. long, and although this length of tube minimises the errors consequent on the use of a short tube, it has many manipulative disadvantages. The value of the velocity of retrogression was obtained from the equation $C = 1 \div (t_2 - t_1) \times \log \{(\beta_1 - \phi)/(\beta_2 - \phi)\}$ where ϕ is the final rotation and β_1 and β_2 that after times t_1 and t_2, a form of expression which does not necessitate a knowledge of the absolute values of t_1 and t_2. The values so obtained with pure water are 0·00637 (T = 20·25°) and 0·00610 (T = 20·1). Researches are next recorded with acetic, propionic, sulphuric, nitric, hydrochloric, chloracetic, dichloracetic, and trichloracetic acids in N/10, and frequently, also, N/50 solutions. The velocity is found to be dependent on the nature and concentration of the acid, and the intimate connection between this effect of the acid and its affinity constant is seen in the accompanying table.

Acid.	1.	2.	3.	4.
Hydrochloric	100·00	100·0	100·0	100·0
Nitric	98·99	99·6	91·0	100·0
Trichloracetic	96·67	62·3	68·2	75·4
Sulphuric	71·95	65·1	73·9	73·2
Dichloracetic	62·41	25·3	23·0	27·1
Monochloracetic	17·25	4·9	4·3	4·84
Acetic	4·70	1·42	0·345	0·4
Propionic	1·63	0·32	0·304	—

1 is the effect on multirotation; 2, electrical conductivity; 3, catalysis of methylic acetate; 4, inversion of cane sugar.

Alcohol, as expected, causes a decrease of the velocity, as does also sodium chloride; sodium sulphate, however, causes a marked increase,

due, the author considers, to a partial decomposition, $Na_2SO_4 + OH_2 = NaHSO_4 + NaOH$, this view being further supported by the great accelerating influence of sodium salts of feeble acids, such as sodium acetate. Strong bases cause so rapid a decrease of the rotation that they are practically unmeasurable; ammonia, however, was measured, and found to cause an acceleration, but not as great as that due to strong acids. L. M. J.

Combination of Iodine with Potato Starch. By GASTON ROUVIER (*Compt. rend.*, 1895, **120**, 1179—1180).—The maximum quantity of iodine with which potato starch will combine is 18·6 per cent., even when the iodine is present in very large excess. In the case of wheat and rice starch, the maximum is 19·6 per cent. In presence of water, the potato starch combines with only 13·5 per cent. of the iodine, the corresponding number in the case of wheat and rice being about 8·9. When the quantity of iodine added to a given weight of starch is gradually increased, the proportion entering into combination also gradually increases up to the maximum, but the variations are less rapid than with wheat starch and rice starch (Abstr., 1894, i, 63 and 353).

It would seem that whilst starches of the same class, such as wheat starch and rice starch, behave similarly in contact with iodine, starches derived from plants belonging to different families behave very differently. C. H. B.

Oxidation of Complex Carbohydrates. By GUILLAME DE CHALMOT (*Amer. Chem. J.*, 1895, **17**, 535—539).—The action of soda and bromine on certain carbohydrates was tried. From starch, a product is formed which reduces Fehling's solution in the cold; cellulose yields apparently an oxycellulose which reduces Fehling's solution at 100°; the products obtained from saccharose and from α-methyl-*d*-glucoside gave respectively glucosazone and a substance which was the osazone either of α-methyl-*d*-glucoside or of *d*-glucose. C. F. B.

Aliphatic Nitramines. By H. VAN ERP (*Rec. Trav. Chim.*, 1895, **14**, 1—55).—A study of the butylnitramines and normal hexylnitramines. The starting point in each case was the corresponding monalkylamine, which was converted into the methylic or ethylic alkylcarbamate, and the latter nitrated; the alkylic nitrocarbamate was then decomposed with ammonia, and the ammonium derivative of the nitramine thus formed was decomposed by dilute sulphuric acid.

Normal butylamine was prepared by reducing butyronitrile with sodium in alcoholic solution, the nitrile being obtained by the successive distillation of butyric acid with ammonium thiocyanate, and of the resulting product with phosphoric anhydride. The tertiary butylamine and the hexylamine were made respectively from trimethylacetamide and normal heptoamide by the action of bromine and alkali, the trimethylacetic acid being obtained by oxidising pinacoline with chromic acid. Normal hexylamine may be characterised by means of *dinitrohexylaniline*, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}C_6H_{13}$, from 1 : 2 : 4-bromodinitrobenzene, and by the corresponding *trinitro-compound*

from picryl chloride. The former compound crystallises in long, slender, yellow needles, and melts at 38·2—39·2°, whilst the latter forms large, yellow, doubly-refracting plates belonging to the asymmetric system, and melts at 70—70·5°; $\alpha = 91° 56'$; $\beta = 124° 10'$; $\gamma = 82° 54'$.

A bye-product obtained in the preparation of the tertiary butylamine was probably *symmetrical ditertiarybutylcarbamide*,

$$CO(NH\cdot CMe_3)_2.$$

This is a micro-crystalline powder insoluble in water, but soluble in alcohol and ether; it sublimes at 250° without melting.

The carbamates were obtained by adding methylic or ethylic chlorocarbamate to a mixture of the respective amines with aqueous potash, and extracting the product with ether. They are colourless, viscid liquids, having for the most part faint, ethereal odours. The yields were good. *Methylic butylcarbamate*, NHBu·COOMe, melts at −18·5° to −17·5°, and boils at 92° (15 mm.); sp. gr. = 0·974 at 15°; the *ethylic* salt melts at −22·5° to −21·5°, and boils at 100° (15 mm.); sp. gr. = 0·951 at 15°. *Methylic secondary butylcarbamate*, CHMeEt·NH·COOMe, boils at 83° (16 mm.); sp. gr. = 0·972 at 15°; the *ethylic* salt melts at −14° to −13° and boils at 89·8° (15 mm.); sp. gr. = 0·9495 at 15°. *Methylic isobutylcarbamate*, $CH_2Pr^{\beta}\cdot NH\cdot COOMe$, melts at −23·5° to −21°, and boils at 89° (18 mm.); sp. gr. = 0·9695 at 15°; the *ethylic* salt boils at 96° (17 mm.), and does not solidify at −65°; sp. gr. = 0·9465 at 15°. *Methylic tertiary butylcarbamate*, $CMe_3\cdot NH\cdot COOMe$, melts at 26·7—27·2°, and boils at 63·3° (17 mm.); sp. gr. = 0·966 at 15°; the *ethylic* salt melts at 20·5—22°, and boils at 72° (16 mm.); sp. gr. = 0·943 at 15°; the odour of both these salts resembles that of menthol. *Ethylic hexylcarbamate*, $C_6H_{13}\cdot NH\cdot COOEt$, boils at 232—234° (uncorr.), and has sp. gr. = 0·915 at 15°; the melting point of a second preparation, sp. gr. = 0·9231 at 15°, was −6·7°.

The nitrocarbamates are prepared by adding the carbamates to concentrated nitric acid at 0°, or, in some cases, at still lower temperatures; the product is poured on to a mixture of sodium carbonate crystals and ice, and the oily carbamate taken up with ether. There is no oxidation in the case of the primary and isoprimary compounds, but the secondary butyl derivatives are prepared only with great difficulty, and the tertiary compound could not be prepared at all. The yields were almost theoretical. The nitrocarbamates are nearly colourless, oily liquids of faint ethereal or aromatic odour. They solidify at low temperatures to crystalline or porcelain-like masses, and apparently cannot be distilled without decomposing. *Methylic butylnitrocarbamate*, $NO_2\cdot NBu\cdot COOMe$, melts at −35·2° to −34·2°; sp. gr. = 1·149 at 15°; the *ethylic* salt is still liquid at −70°; sp. gr. = 1·1055 at 15°. *Methylic secondary butylnitrocarbamate*, $CHMeEt\cdot N(NO_2)\cdot COOMe$, becomes viscid at −70°; sp. gr. = 1·1355 at 15°; the *ethylic* salt remains liquid at −70°; sp. gr. = 1·094 at 15°. *Methylic isobutylnitrocarbamate*, $CH_2Pr^{\beta}\cdot N(NO_2)\cdot COOMe$, melts at 2°; sp. gr. = 1·144 at 15°; the *ethylic* salt becomes very slightly viscid at −75°; sp. gr. = 1·101 at 15°. *Ethylic hexylnitro-*

carbamate, $C_6H_{13}\cdot N(NO_2)\cdot COOEt$, solidifies at −60°, and melts at −45° to −40°; sp. gr. = 1·062 at 15°.

The nitramines are prepared by saturating the dry, ethereal solutions of the methylic or ethylic nitrocarbamates with dry ammonia, the resulting crystalline ammonium salt of the nitramine being decomposed with dilute sulphuric acid, and the amine separated partly mechanically and partly by extraction with ether; the yield was in most cases almost theoretical. The nitramines are colourless, somewhat viscid liquids, having little odour; they are only sparingly soluble in water, but easily in the usual organic solvents; the aqueous solutions are alkaline to litmus. They readily dissolve in alkalis, forming salts from which various metallic and alkylic salts can be prepared. It is noteworthy that both butyl- and isobutyl-nitramines form two methylic derivatives, to which apparently the same structure must be assigned. *Butylnitramine*, $NHBu\cdot NO_2$, melts at −0·5° to +0·5°; sp. gr. = 1·0665 at 15°; the *ammonium* derivative crystallises in small, white, glistening scales, and superficially dissociates in air into its proximate constituents; the *potassium*, *barium*, and *silver* derivatives are crystalline. The two *methyl* derivatives are prepared respectively from the potassium compound by the action of methylic iodide and methylic alcohol, and from the silver derivative by means of methylic iodide in ethereal solution. *α-Methylbutylnitramine*, $NMeBu\cdot NO_2$, has an odour of menthol; it boils at 107·7° (15 mm.), and is still liquid at −30°; sp. gr. = 1·031 at 15°; *β-Methylbutylnitramine*, $NMeBu\cdot NO_2$ (?), has, on the other hand, a very pungent odour; it boils at 75—88°; sp. gr. = 0·9865 at 15°. *Secondary butylnitramine*, $CHMeEt\cdot NO_2$, melts at −34·5° to −33°; sp. gr. = 1·066 at 15°; the *ammonium*, *barium*, and *silver* derivatives are crystalline, but neither the *potassium* nor the sodium derivative could be crystallised; the former is very hygroscopic. *Isobutylnitramine*, $CH_2Pr^{\beta}\cdot NH\cdot NO_2$, is a white, crystalline substance, and melts at 32·2°; sp. gr. = approximately 1·142; the *ammonium* and *silver* derivatives are crystalline; the *potassium* derivative crystallises with 1 mol. H_2O, which it loses at 125°, and the anhydrous compound decomposes at 245° without melting. The two *methylic* derivatives were prepared in the same way as those of the normal butyl derivatives; *α-methylisobutylnitramine* forms small, colourless crystals, and resembles the corresponding normal compound in odour; it melts at 22·4°, and boils at 104—104·2° (17 mm.). *β-Methylisobutylnitramine* also resembles the corresponding normal compound in odour; it boils at 63—66° (17 mm.), and is still liquid at −20°.

Hexylnitramine, $C_6H_{13}\cdot NH\cdot NO_2$, melts at 5·5—6·5° to a colourless liquid, of sp. gr. = 1·014 at 15°; the *ammonium* derivative forms colourless, greasy scales, and is very soluble in water; the *potassium* derivative is crystalline, and commences to melt at 230°, but the melting is not complete at the temperature, 280°, at which decomposition sets in. The *silver* and *cobalt* derivatives are crystalline.

The specific gravities of the alkyl nitramines and nitrocarbamates, as of other homologous compounds, diminish as the series is ascended; the relations between the melting points of the various isomeric butyl compounds are normal.

Hexylnitramine is completely decomposed by dilute sulphuric acid into two hexylic alcohols, a hexylic ether, a hexylene, and nitrous oxide. The *hexylene*, probably $CHBu^{\alpha}{:}CH_2$, is a colourless, mobile, and extremely volatile liquid, resembling light petroleum in odour; it boils at 67·5—68·5° and has a sp. gr. of 0·683 at 15°. The corresponding *dibromohexane*, probably $CHBuBr{\cdot}CH_2Br$, is a colourless liquid, of agreeable ethereal odour, and decomposes when distilled, to some extent even under diminished pressure. It boils at 90—93° (18 mm.); sp. gr. = 1·604 at 15°. One of the hexylic alcohols was identified as the normal primary alcohol; the other, which boiled at 140—142°, and had a sp. gr. of 0·819 at 15°, yielded a blue pseudonitrole, and was therefore a *secondary alcohol*, probably methylbutylcarbinol. The *dihexylic ether* boiled at 218—221°.

The decomposition, as far as regards the formation of the primary alcohol, resembles that of the nitrites and nitroso-derivatives of the amines, but the mechanism of the formation of the secondary alcohol and the olefine has yet to be explained, for neither of these products can be formed from the other under the conditions under which they are formed from the nitramine. It is possible that the nitramine is simply resolved into the olefine and free nitramide, $NH_2{\cdot}NO_2$, and that part of the nitrous oxide is due to the decomposition of the latter.

The monalkylnitramines and those dialkylnitramines, such as diethyl- and dipropyl-nitramine, which do not contain a methyl group, are stable towards alkalis, but the methylalkylnitramines are decomposed by aqueous potash in a complex manner. Dimethylnitramine, for example, yields methylamine, nitrous acid, and formic acid, together with a small amount of dimethylamine, and probably some methylic alcohol. Methylbutylnitramine yields, but with greater difficulty, butylamine and formic and nitrous acids. JN. W.

Hexamethylenetetramine Salts. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], **13**, 352—355).—Hexamethylenetetramine crystallises in forms which belong either to the cubic system or to a closely approximating rhombohedral system; the crystals, which are formed equally well from aqueous and alcoholic solutions, are extremely clear, and highly refractive. The amine is soluble in all the usual solvents with the exception of ether; the percentage solubilities at 12° being 81·30 for water, 3·22 for alcohol, and 8·09 for chloroform.

The *hydrate*, $C_6H_{12}N_4 + 6H_2O$, separates in very large striated prisms when the aqueous solution is exposed to temperatures about 0°; it melts below 15°, but as the quantity of water liberated is insufficient to retain the whole of the amine in solution, a portion of the latter is precipitated in the anhydrous state. The hydrobromide crystallises in brilliant rhombehedra, $\alpha : \beta : \gamma : \delta = 1 : 1 : 1 : 1{\cdot}034$. The *sulphate*, $C_6H_{12}N_4,H_2SO_4 + H_2O$, is a white, crystalline powder, which melts at 108°, boils and probably decomposes at 130—140°, and solidifies and melts again at about 188°; it is stable at 100°. The *phosphate*, $5C_6H_{12}N_4,6H_3PO_4 + 10H_2O$, forms white colourless, nacreous crystals, and melts at about 188°, at the same time decomposing. The taste of all three of these salts is extremely acid, and it

is noteworthy that their melting points are all in the neighbourhood of the temperature at which the amine itself decomposes.

JN. W.

Hexamethylenetetramine Bismuthiodides. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], **13**, 351—352).—A fourth *bismuthiodide*, $(C_6H_{12}N_4{\cdot}HI)_5(BiI_4H)_3 + 4H_2O$, is obtained by adding the amine to an excess of the product of the action of acid bismuth sulphate on potassium iodide; it is a dense, orange-yellow microcrystalline precipitate, which, after remaining for several months in contact with the original solution, is transformed into needles of a somewhat redder shade. When heated at 100°, it loses water and becomes still darker in colour, but the dehydrated substance gradually reabsorbs the water on exposure to moist air. JN. W.

Action of Methylic Iodide on Dimethylasparagine. By W. KORNER and ANGELO MENOZZI (*Gazzetta*, 1895, **25**, i, 97—100).—The behaviour towards methylic iodide of the dimethylasparagine previously prepared by the authors (Abstr., 1890, 869) is completely analogous to that of asparagine itself; when heated with methylic alcoholic potash and methylic iodide, it yields tetramethylammonium iodide and *methylfumaramic acid*, NHMe·CO·CH:CH·COOH. The new acid crystallises from water in anhydrous prisms melting at 208°, and yields methylamine and fumaric acid on boiling with aqueous potash; its *potassium* salt separates from water in lustrous, anorthic prisms; $a : b : c = 0{\cdot}692 : 1 : 0{\cdot}441$. $\alpha = 85° 32'$, $\beta = 94° 56'$, $\gamma = 73° 19'$. The *sodium* salt crystallises in transparent laminæ, the *silver* salt is an insoluble, amorphous powder, and the *methylic* salt crystallises in transparent needles melting at 138°.

The acid described by Giustiniani as methylfumaramic acid (Abstr., 1892, 821), if pure, cannot have the same constitution as the above, owing to the differences between the melting points and habits. W. J. P.

Glutarimide. By R. SELDNER (*Amer. Chem. J.*, 1895, **17**, 532—535).—Glutarimide, $CH_2<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>NH$, is formed by heating together in sealed tubes at 200—210°, glutaric acid (1 mol.) and acetonitrile (2 mols.), or glutaronitrile (1 mol.) and acetic acid (2 mols.), or glutaric acid (1 mol.) and glutaronitrile (1 mol.), a drop or two of acetic anhydride being added to each tube. The last method gives the best yields, in the two others, the glutarimide is mixed with acetic acid and acetonitrile. C. F. B.

Addition of Bromine to Tetrolic acid. By ADOLF PINNER (*Ber.*, 1895, **28**, 1877—1887).—The author has previously stated (Abstr., 1881, 793) that tetrolic acid forms a dibromide, which melts at 95—97°. Michael and Pendleton (Abstr., 1888, 1176) have since prepared the same dibromocrotonic acid, and give 94° as the melting point, whilst Fittig and Clutterbuck, by the addition of bromine to tetrolic acid, obtained a dibromocrotonic acid which melted at 120°, but were unable to prepare the acid melting at 94°.

The author has re-examined his acid and finds that it melts at 94°, and not at 95—97° as originally stated; he also finds that his acid is entirely different in crystallographic properties from the acid described by Fittig and Clutterbuck.

It is now shown that the product obtained by the action of bromine on tetrolic acid depends not only on whether the operation is carried out in sunlight or in the dark, but also on the solvent used. Bromine (2 atoms) acts on a cooled aqueous solution of tetrolic acid, forming the dibromocrotonic acid which melts at 120°, together with a small quantity of acraldehyde; if, however, the bromine is added in the dark, the dibromocrotonic acid, of melting point 94°, is formed. Bromine acts in much the same way on tetrolic acid in a chloroform solution cooled to 0°. Even when excess of bromine is employed, one of the dibromocrotonic acids is the product formed, but if carbon tetrachloride is used as the solvent, and the bromination is carried on in direct sunlight, hydrogen bromide is evolved, and the main product is tribromocrotonic acid (m. p. 131°), compare Fittig (*Annalen*, 1892, **268**, 107). When the bromine is added to the carbon tetrachloride solution in the dark, no hydrogen bromide is evolved, and the product is a mixture of the two isomeric dibromocrotonic acids. The author regards these two acids as stereoisomeric.

Me·C·Br ‖ COOH·C·Br	Me·C·Br ‖ Br·C·COOH
M. p. 94°.	M. p. 120°.

The acid with the lower melting point is the less stable. Its salts, when heated with water, lose carbonic anhydride and hydrogen bromide, and then form acraldehyde. When hydrogen bromide is passed into a concentrated benzene solution of the acid of lower melting point, it is converted into the isomeric acid of higher melting point.

Tetrabromocrotonic acid is obtained when either of the dibrom-acids is dissolved in carbon tetrachloride and treated with bromine in direct sunlight. It crystallises in large, glistening prisms, melts at 146°, and is readily soluble in water or benzene, but only sparingly in carbon tetrachloride, and still more sparingly in light petroleum. The tetrabrom-acid, and also the two dibrom-acids, when treated with sodium amalgam, yield tetrolic acid. If the tetrbrom-acid is neutralised with dilute ammonia, and silver nitrate is added to the solution, decomposition takes place, silver bromide is thrown down, and mucobromic acid, COOH·CBr:CBr·CHO, remains in solution.

J. J. S.

Mixed Anhydrides. By L. Rousset (*Bull. Soc. Chim.*, 1895, [3], **13**, 330—334).—The mixed anhydrides of the type R·CO·O·CO·R′ do not appear to exist, as their boiling points are indefinite, and they are readily resolved, by fractional distillation, into mixtures, in molecular proportion, of the corresponding simple anhydrides.

Thus the product of the action of acetic chloride on sodium butyrate is a mixture of acetic and butyric anhydrides; Autenrieth's acetovaleric anhydride, from sodium acetate and valeric chloride, is a mixture of acetic and valeric anhydrides, and the product of the

action of benzoic chloride on sodium acetate is a mixture of acetic and benzoic anhydrides.

The instability of the mixed anhydrides affords a convenient means of preparing anhydrides from acid chlorides. The latter are simply heated with sodium acetate, and the mixtures of anhydrides thus obtained is separated by fractional distillation. JN. W.

Etherification and Hydrolysis. By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 1913—1914).—A claim of priority.

Ozobenzene. By ADOLPHE RENARD (*Compt. rend.*, 1895, **120**, 1177—1179).—In order to obtain ozobenzene (this Journal, 1873, 610), the benzene must be carefully purified, and the current of ozone must be well dried. When the benzene contains thiophen, only the dark-coloured, non-explosive substance, described by Leeds (*Ber.*, **14**, 975), is formed.

Ozobenzene, when freed from excess of benzene by means of a current of dry air, is a white, amorphous substance, which explodes violently on the slightest friction and detonates if heated rapidly to 50°, but decomposes without exploding if very slowly heated. It also detonates in contact with concentrated sulphuric acid, ammonia, or aqueous potash. It remains unchanged in dry air, but decomposes in contact with moist air. In contact with water, it decomposes slowly, with evolution of carbonic anhydride and formation of acetic and formic acids. By weighing the carbonic anhydride evolved, and burning in the usual way the other products of the action of water, it is found that ozobenzene has the composition $C_6H_6O_6$. Ozobenzene is insoluble in most organic solvents, but dissolves in acetic acid.

C. H. B.

Action of Acid Chlorides on α-Hexachlorophenol in Presence of Aluminium Chloride. By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], **13**, 340—345).—When aluminium chloride is added to a cooled carbon bisulphide solution containing α-hexachlorophenol and an acid chloride, there is a slight elevation of temperature, but no evolution of hydrogen chloride, and crystals of an additive metallic compound can be separated from the product (see following abstract); at a higher temperature, however (35—40°), a violent action takes place, hydrogen chloride is evolved, and a nearly quantitative yield of crystals of the acidyl derivative of pentachlorophenol is obtained. The crystalline product, after being drained, is digested with cold water to decompose the sulphur chloride formed in the action, and the dry substance is recrystallised from benzene or light petroleum.

Pentachlorophenylic acetate, $C_6Cl_5{\cdot}OAc$, crystallises in long, slender, monoclinic prisms, and melts at 149·5—150·5°, not at 148—149° as stated by Weber and Wolff; it remains practically unaffected by boiling with concentrated aqueous potash, but is completely hydrolysed by alcoholic potash at 120°. The *propionate* forms long, soft, white, silky needles, and melts at 78·5°. It is easily hydrolysed by alkalis. The *butyrate* separates from light petroleum as a felted mass of fine, white, soft needles; it softens at 49° and melts at 59—62·5°, but the product obtained was not quite pure, as the compound is

hydrolysed, even by moist air, into its proximate constituents. The *benzoate* crystallises in colourless, highly refractive, monoclinic prisms, sp. gr. = 1·711 at 18°, and melts at 159—160°. It is stable towards strong, boiling, aqueous potash, but is hydrolysed by alcoholic potash at 120°.

It is probable that the sulphur chloride and the carbon sulphochloride formed in the preparation result from the action of nascent chlorine on the carbon bisulphide, this chlorine being produced, together with the compound $C_6Cl_5{\cdot}O{\cdot}Al_2Cl_5$, by the decomposition of the original additive compound. Jn. W.

Action of Aluminium Chloride on α-Hexachlorophenol. By Etienne Barral (*Bull. Soc. Chim.* 1895, [3], **13**, 345—348).—When α-hexachlorophenol is heated with aluminium chloride ($\frac{1}{8}$ mol.) in sealed tubes at 160—165°, the chief products are pentachlorophenol and chloranil. With more of the chloride ($\frac{1}{2}$ mol.), and at 170—175°, much carbonyl chloride is formed, and the principal product is hexachlorobenzene, whilst with the same proportion of the chloride, and in presence of carbon bisulphide, a reaction occurs similar to that described in the preceding abstract, pentachlorophenol, sulphur chloride, and carbon sulphochloride being formed; at a higher temperature, however, a small quantity of *pentachlorophenylic carbonate*, $CO(O{\cdot}C_6Cl_5)_2$, is produced. This forms very small, colourless, nacreous crystals, which begin to sublime at about 250° and melt at 265—268°; it can be volatilised without decomposing. Jn. W.

Preparation of Orthodibromaniline. By W. Korner (*Gazzetta*, 1895, **25**, i, 95—97).—Orthodibromaniline [$NH_2 : Br_2 = 1 : 3 : 4$] is readily prepared by acetylating metabromaniline with acetic anhydride and brominating the resulting metabromacetanilide in acetic acid solution; it melts at 80·4—80·5°, and gives crystalline salts. The *monacetyl* derivative, $C_6H_3Br_2{\cdot}NHAc$, crystallises in thin prisms melting at 128°, and the *diacetyl* derivative, $C_6H_3Br_2{\cdot}NAc_2$, forms lustrous scales, melting and decomposing at 208°. This dibromaniline is violently acted on when warmed with alcoholic ethylic nitrite, nitrogen being evolved and orthodibromobenzene being produced. W. J. P.

Conversion of an Aniline Salt into an Anilic acid. By Louis Simon (*Compt. rend.*, 1895, **120**, 1174—1177).—Pyruvic acid and aniline do not form aniline pyruvate, but only *anilpyruvic acid*, which seems to be a consequence of the presence of the ketonic function. On the other hand, phenylglyoxylic acid yields exclusively the ordinary salt. It would seem, however, that this difference is more apparent than real, for, although aniline phenylglyoxylate when heated loses carbonic anhydride and water and is converted into benzylideneaniline, CHPh:NPh, when dissolved in cold methylic alcohol, or when boiled with chloroform or benzene, it is completely converted into *anilphenylglyoxylic acid*, NPh:CPh·COOH, a white, crystallisable compound, melting and decomposing at 151° with formation of the compound CHPh:NPh. Anilphenylglyoxylic acid

is insoluble in boiling benzene or chloroform, and only slightly soluble in ether or cold acetic acid. When boiled with water, it is completely reconverted into aniline phenylglyoxylate. It also dissolves in acids and alkalis. Aniline phenylglyoxylate yields an abundant precipitate with phenylhydrazine, but anilphenylglyoxylic acid does not, and this is a further proof that the ketonic function existing in the one is non-existent in the other.

Ammonia and the toluidines yield similar results. C. H. B.

Benzenesulpho-orthotoluidide and its Derivatives. By CH. RABAUT (*Compt. rend.*, 1895, **120**, 1123—1126).—*Benzenesulpho-orthotoluidide*, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4Me$, is obtained by heating benzenesulphonic chloride (1 mol.) with orthotoluidine (2 mols.), in presence of benzene or strong alcohol. It separates from alcohol in white crystals, which melt at 122—123°, and boil without decomposing at about 290—295° under a pressure of 50 to 60 mm. It is insoluble in water, but dissolves in alkalis and organic solvents. When boiled with nitric acid of sp. gr. 1·10, it yields a yellow dinitro-derivative, $SO_2Ph\cdot NH\cdot C_6H_2Me(NO_2)_2$, which melts at 167—168°. Under similar conditions acetylorthotoluidine is completely decomposed into acetic acid and toluidine.

The dinitro-derivative, when heated in sealed tubes at 140° with concentrated hydrochloric acid, yields a dinitrotoluidine,

$$[Me : NH_2 : NO_2 : NO_2 = 1 : 2 : 3 : 5],$$

which melts at 208—209°, and was described by Städel (Abstr., 1881, 724). When treated by Prud'homme and Rabaut's method (Abstr., 1892, 705), it yields the chloride $C_6H_2Me(NO_2)_2Cl$ [Me : Cl : NO_2 : NO_2 = 1 : 2 : 3 : 5], which forms yellow crystals melting at 45—46°.

It follows that the original dinitro-derivative has the constitution [Me : NO_2 : NO_2 : $NH\cdot SO_2$ = 1 : 3 : 5 : 6], the two benzene nuclei being linked by the group $SO_2\cdot NH$. It has strongly marked acid properties, dissolves in alkalis, and decomposes barium carbonate at 100°, forming a barium salt which separates in yellow crystals; these lose 1 mol. H_2O at 140°, and only decompose at about 215°. Hydrochloric acid precipitates the dinitro-derivative, which can thus be purified. Reduction with tin and hydrochloric acid yields the diamine in white needles, which melt at 217° and turn red when exposed to air. It forms salts very soluble in water, and is readily diazotised.

The general stability of benzenesulpho-orthotoluidide, notwithstanding its amide character, is especially noteworthy.

C. H. B.

Reduction by means of Phenylhydrazine. By R. WALTHER (*J. pr. Chem.*, 1895, [2], 141—144).—The author draws attention to the application of phenylhydrazine as a reducing agent in organic chemistry; such reductions as that of azobenzene to hydrazobenzene, and that of nitro-compounds to the corresponding amido-derivatives being easily effected by its means. A. G. B.

Isohydroxydiphenylethylamine from Glycocine and Benzaldehyde. By EMIL ERLENMEYER, Jun. (*Ber.*, 1895, **28**, 1866—1869).—The author has previously shown (Abstr., 1893, i, 166) that benzaldehyde and glycocine, in dilute alcoholic solution and in presence of sodium hydroxide, condense to form a sodium salt,

$$OH\cdot CHPh\cdot CH(N{:}CHPh)\cdot COONa,$$

and a substance soluble in alcohol. The latter has since been investigated, and is now shown to have the composition

$$OH\cdot CHPh\cdot CHPh\cdot N{:}CHPh.$$

When treated with hydrochloric acid, it is decomposed into benzaldehyde and *isohydroxydiphenylethylamine;* this base, which melts at 128°, stands in the same relation to the diphenylhydroxyethylamine (m. p. 161°) of Goldschmidt and Polonowska (Abstr., 1887, 492) as isohydrobenzoïn does to hydrobenzoïn. If distilled with zinc dust, it yields stilbene; when oxidised, it gives benzile, and when diazotised and converted into the corresponding glycol, it yields isohydrobenzoïn; if heated to about 130°, it decomposes into benzaldehyde and benzylamine. The original condensation product can be regenerated by heating isodiphenylhydroxyethylamine with benzaldehyde in alcoholic solution. The author regards his base and isohydrobenzoïn as the true analogues of racemic acid, on account of the hemimorphic character of their crystals; whereas hydroxydiphenylethylamine and hydrobenzoïn are the analogues of mesotartaric acid. J. J. S.

Heterocyclic Bases from Hydroxydiphenylethylamine. By HENRYK G. SÖDERBAUM (*Ber.*, 1895, **28**, 1897—1903).—The carbamide and thiocarbamide derivatives obtained by treating hydroxydiphenylethylamine respectively with isocyanates and thiocarbimides readily yield condensation products according to the scheme

$$\begin{matrix} CHPh\cdot NH\cdot CO\cdot NHR \\ | \\ CHPh\cdot OH \end{matrix}^{(S)} = H_2O + \begin{matrix} CHPh\cdot N \\ | \\ CHPh\cdot O \end{matrix}\!\!>\!C\cdot NHR.\ {}^{(S)}$$

These condensation products are strongly basic, forming salts which are not decomposed by water; they also yield crystalline platinochlorides, which are for the most part sparingly soluble. They greatly resemble the amidobenzoxazoles (amidobenzothiazoles), but are totally different from the isomeric β-oximidazoles, and are to be regarded as derivatives of the compound $\begin{matrix} {}^{(4)}CH_2\cdot N \\ | \\ CH_2\cdot O \end{matrix}\!\!>\!C\cdot NH_2$ $\begin{matrix} {}^{(2)} \\ {}^{(5)}\ {}^{(S)} \end{matrix}$, which the author terms *dihydroamidoazoxole* (*dihydroamidoazthiole*).

Hydroxydiphenylethylcarbamide, $OH\cdot CHPh\cdot CHPh\cdot NH\cdot CO\cdot NH_2$, is obtained from hydroxydiphenylethylamine hydrochloride and potassium cyanate in aqueous solution. It forms colourless crystals, melts at 215°, and is insoluble in water and ether, but dissolves in acetone and hot alcohol.

4 : 5-*Diphenyldihydro*-2-*amido*-1 : 3-*azoxole* is obtained when the preceding compound is heated with dilute hydrochloric acid for

1—2 hours, and the solution precipitated with sodium hydroxide. It crystallises in six-sided needles, and melts at 153—154°. The platinochloride, $(C_{15}H_{14}N_2O)_2,H_2PtCl_6$, forms minute, yellowish crystals, and melts at 203°.

Methylhydroxydiphenylethylthiocarbamide,

$$OH\cdot CHPh\cdot CHPh\cdot NH\cdot CS\cdot NHMe,$$

obtained from hydroxydiphenylethylamine and methylthiocarbimide, forms colourless plates which melt at 136°.

4 : 5-*Diphenyldihydro*-2-*methylamido*-1 : 3-*azoxole* is obtained by treating the preceding compound in alcoholic solution with yellow mercuric oxide; it forms colourless, glistening needles, and melts at 158—159°. The platinochloride, $(C_{16}H_{16}N_2O)_2,H_2PtCl_6$, crystallises in minute, yellowish plates which decompose at 215°.

4 : 5-*Diphenyldihydro*-2-*methylamido*-1 : 3-*azothiole*, when recrystallised from alcohol, forms large, colourless prisms, and melts at 155°. The *platinochloride* $(C_{16}H_{16}N_2S)_2,H_2PtCl_6$, crystallises in yellowish-red prisms which undergo decomposition at 220°.

Ethylhydroxydiphenylethylthiocarbamide,

$$OH\cdot CHPh\cdot CHPh\cdot NH\cdot CS\cdot NHEt,$$

crystallises in small needles, and melts at 148—149°. When treated with mercuric oxide, it yields 4 : 5-*Diphenyldihydro*-2-*ethylamido*-1 : 3-*azoxole*, which melts at 141°; its *platinochloride*,

$$(C_{17}H_{18}N_2O)_2,H_2PtCl_6,$$

crystallises in yellowish prisms, and melts at 195—200°. The corresponding *azothiole*, $C_{17}H_{18}N_2S$, melts at 139°, and forms a *platinochloride* which melts at 185—188°.

Phenylhydroxydiphenylethylcarbamide,

$$OH\cdot CHPh\cdot CHPh\cdot NH\cdot CO\cdot NHPh,$$

prepared from hydroxydiphenylethylamine and phenylthiocarbimide, forms colourless crystals, and melts at 176°; the corresponding *phenylhydroxydiphenylethylthiocarbamide* melts at 171°, and when treated with mercuric oxide yields 4 : 5-*diphenyldihydro*-2-*phenylamido*-1 : 3-*azoxole*, which crystallises in small, white needles and melts at 162—163°; its *platinochloride*, $(C_{21}H_{18}N_2O)_2,H_2PtCl_6 + 3H_2O$ forms yellow, glistening needles, which undergo decomposition at 195—198°.

Orthotolylhydroxydiphenylethylthiocarbamide,

$$OH\cdot CHPh\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot C_7H_7,$$

crystallises from toluene in short, white needles, which melt at 156—157°. When treated with mercuric oxide, it gives 4 : 5-*diphenyldihydro*-2-*orthotolylamido*-1 : 3-*azoxole*, which melts at 136—138°; its *platinochloride*, $(C_{22}H_{20}N_2O)_2,H_2PtCl_6$, melts at 220—225°.

J. J. S.

Aromatic Nitroso-bases. By Otto Fischer (*Annalen*, 1895, **286**, 145—186).—In a short introduction, the author discusses the constitution of aromatic nitroso-bases.

By Otto Fischer and E. Schäffer.—The *hydrochloride of paranitrosoaniline*, $C_6H_6N_2O,HCl$, separates from alcohol in dark brown crystals; the *sulphate* crystallises in yellowish-white prisms. The *oxalate* forms small, greenish crystals, and the *picrate* separates as a brown mass of crystals on adding ether to the alcoholic solution. The *dibenzoyl* derivative crystallises in dark brown needles or leaflets, and melts at 142°; in preparing it, it is necessary to dissolve the nitrosoaniline in a dilute solution of sodium hydroxide and agitate the cold liquid with excess of benzoic chloride; otherwise, if strong soda is used and the mixture is allowed to get warm, benzoylnitrosophenol is formed. *Orthohydroxybenzylideneparanitrosoaniline* is prepared by heating the base with salicylaldehyde for two hours at 100°; it softens at 235°, and melts at 245°. Paranitraniline is formed when paranitrosoaniline is oxidised with potassium permanganate, whilst reducing agents give rise to paraphenylenediamine.

By Otto Fischer and H. Apitsch.—The *picrate of paranitrosoethylaniline* crystallises from water in dark yellow needles, and melts at 131°; the *silver* salt, which has the composition $3C_8H_{10}N_2O,AgNO_3$, separates in small, dark green, lustrous crystals, and melts and decomposes at 121°. The *mercurochloride* melts and decomposes at 142°.

The nitrosamine of paranitrosoethylaniline is very stable in presence of reducing agents. With acetic acid and zinc-dust, a colourless oil is obtained, which gives Liebermann's reaction; on adding sodium amalgam to the cold alcoholic solution of the nitrosamine, the liquid becomes reddish-brown, and a yellow precipitate is formed, which, when recrystallised from alcohol, melts at 171°. This *compound* has the formula $C_{16}H_{18}N_6O_3$, and gives Liebermann's reaction; on reduction, it yields ethylparaphenylenediamine.

α-Nitroso-α-methylnaphthylamine, $C_{10}H_6{\ll}^{NHMe}_{N\text{——}}{>}O$, is prepared by dissolving α-methylnaphthylamine in dilute sulphuric acid, adding sodium nitrite, and extracting with ether; the nitrosamine, which is left as a viscid oil on evaporation of the ether, is converted into the *hydrochloride* of nitrosomethylnaphthylamine by treatment with alcoholic hydrochloric acid; this salt crystallises in slender, pale green needles; the *picrate* crystallises in greenish-yellow needles, and melts and decomposes at 157°. Nitrosomethylnaphthylamine gives the indazine reaction, a blue colouring matter being produced on treating the alcoholic solution of the hydrochloride with diphenylmetaphenylenediamine; this product, symmetrical *anilido-n-methylrosinduline*, $NMe{:}C_{10}H_5{\ll}^{N\text{—}}_{NPh}{>}C_6H_3{\cdot}NHPh$, forms magnificent, golden-green crystals, and melts and decomposes at 225°. The *hydrochloride* was analysed.

When salicylaldehyde is heated with α-nitroso-β-naphthylamine for 2—3 hours on the water bath, a *compound*, $C_{17}H_{12}N_2O_2$, is obtained, which separates from alcohol in green leaflets, and melts at 270° on treating it with boiling acids, salicylaldehyde is formed.

By Otto Fischer and Emil Diepolder.—*Orthonitrobenzylideneorthoparatolylenediamine*, $NHEt{\cdot}C_6H_3Me{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, is obtained

by condensation of monethylorthoparatolylenediamine with orthonitrobenzaldehyde; it crystallises in lustrous, reddish-brown leaflets, and melts at 80°. The *metanitro*-derivative crystallises in yellow needles, and melts at 118°; the *paranitro*-derivative crystallises from alcohol in long, red needles, and melts at 143°. The *orthohydroxy*-derivative crystallises from light petroleum in nodular aggregates of yellow prisms, and melts at 62°. The *thiocarbamide*, $C_{19}H_{26}N_4S$, obtained by boiling carbon bisulphide and a small quantity of alcohol with monethylorthoparatolylenediamine, crystallises from alcohol in small, white needles and melts at 163°. The *benzoyl* derivative of monethylorthoparatolylenediamine crystallises from light petroleum in small needles, and melts at 174°.

The *acetyl* derivative of trimethylmetaphenylenediamine is obtained by heating a solution of acetyldimethylmetaphenylenediamine in xylene with sodium, and, when the metal is dissolved, heating the liquid with methylic iodide; it separates from alcohol in large crystals, and melts at 68°. The *base* boils at 270°, and when its solution, in 10 per cent. sulphuric acid, cooled with ice, is treated with sodium nitrite in dilute aqueous solution, the liquid becomes deep red, and the *dinitrosamine* of dimethylmetaphenylenediamine is precipitated; this crystallises from alcohol in lustrous, brown leaflets, and melts at 109—110°. The quantity of this substance amounts to 5 per cent. of the trimethyl derivative employed, and on extracting the liquor from which it separates with boiling ether, the nitrosamine of trimethylmetaphenylenediamine is obtained; the *hydrochloride* crystallises in colourless leaflets, and on treating it with boiling methylic or ethylic alcohol, a deep red liquid is obtained, and the *monhydrochloride of paranitrosotrimethylmetaphenylenediamine* separates in dark red crystals with green lustre. The *dihydrochloride* crystallises in dark red needles. The base itself, *paranitrosodimethylmetaphenylenediamine*, $NMe_2{\cdot}C_6H_4{\lessdot}^{N}_{N}{>}^{NHMe}_{O}$, crystallises from benzene in long, steel-blue prisms, which appear red by transmitted light, and contain the solvent; it melts at 143°. On adding aqueous sodium nitrite to a solution of the base in dilute sulphuric acid, a *nitro*-derivative of trimethylmetaphenylenediamine nitrosamine is formed, crystallising from ether in yellow needles, and melting at 157°. *Paranitrosodimethylmetaphenylenediamine*,

$$NHMe{\cdot}C_6H_4{\lessdot}^{N}_{N}{>}^{NHMe}_{O},$$

is another product of the action of nitrous acid on trimethylmetaphenylenediamine; after removing the dinitrosamine of dimethylmetaphenylenediamine, the liquid is treated with excess of potassium carbonate, rapidly extracted with ether to remove unaltered trimethylmetaphenylenediamine, and then allowed to remain at the ordinary temperature for 24 hours, the base separating in quantity amounting to 40 per cent. of the substance employed. It crystallises from benzene in steel-blue needles containing the solvent; the *sulphate* crystallises from water in red needles. On reducing to a small bulk the liquid from which the base has been removed, para-

nitrosotrimethylmetaphenylenediamine is obtained: the action of nitrous acid on trimethylmetaphenylenediamine, therefore, gives rise to four products, the nitrosamine of trimethylmetaphenylenediamine, the dinitrosamine of dimethylmetaphenylenediamine, paranitrosotrimethylmetaphenylenediamine, and paranitrosodimethylmetaphenylenediamine.

Symmetrical *dimethylmetaphenylenediamine* is obtained by heating the formyl derivative of monomethylphenylenediamine with sodium methoxide and methylic iodide, and hydrolysing the product with dilute sulphuric acid. It is a colourless oil which, however, rapidly becomes brown; it boils at 165—170° under a pressure of 10 mm., and at 275—280° under a pressure of 739 mm. The dinitrosamine (m. p. 109—110°) is identical with the product of the action of nitrous acid on trimethylmetaphenylenediamine; when it is dissolved in ether, and treated with cold, alcoholic hydrogen chloride, symmetrical *paranitrosodimethylmetaphenylenediamine* is obtained in the form of the hydrochloride. This base separates from ether in magnificent, steel-blue crystals, and melts at 171°.

By Otto Fischer and M. Gmelin.—Paranitrosodiphenylmetaphenylenediamine melts at 153°. When an alcoholic solution of the hydrochloride is heated with aqueous phenylhydrazine hydrochloride at 50—60°, a *compound*, $C_{24}H_{21}N_5$, is formed, which separates from alcohol in pale rose-coloured crystals, and melts at 160°; it is almost insoluble in acids and alkalis, and, when mixed with cupric oxide and heated suddenly, it decomposes explosively.

Formylanilido-n-phenylmethenylphenylenediamine,

$$COH\cdot NPh\cdot C_6H_3<\begin{matrix}NPh\\ __N\end{matrix}>CH,$$

is obtained by heating amidodiphenylmetaphenylenediamine (the reduction product of paranitrosodiphenylmetaphenylenediamine) with concentrated formic acid for several hours; it crystallises from hot, dilute alcohol in colourless needles, and melts at 124°. The *acetylanhydro-base*, obtained from amidodiphenylmetaphenylenediamine by the action of boiling acetic anhydride, has the constitution $NAcPh\cdot C_6H_3<\begin{matrix}NPh\\ __N\end{matrix}>CMe$; it forms colourless crystals, and melts at 165°. *Anilido-n-phenylethenylphenylenediamine*,

$$NHPh\cdot C_6H_3<\begin{matrix}NPh\\ __N\end{matrix}>CMe,$$

is obtained by treating the foregoing compound with boiling dilute sulphuric acid; it crystallises in large, colourless plates melting at 115°, and the *sulphate* crystallises in white leaflets.

When amidodiphenylmetaphenylenediamine is heated on the water bath with salicylaldehyde, a *hydroxybenzylidene* derivative is formed, which crystallises in dark yellow prisms; on recrystallising this substance two or three times from absolute alcohol containing benzene, *anilido-n-phenylorthohydroxybenzenylphenylenediamine* is obtained, crystallising in pale yellow needles, and melting at 190°. The *orthobenzylidene* derivative is brown, being converted into the *anhydro-*

base on recrystallising it from alcohol; this crystallises in orange needles, and melts at 210°. When amidodiphenylmetaphenylenediamine is heated with carbon bisulphide and alcohol for four hours in a reflux apparatus, the *compound* $NHPh\cdot C_6H_3<^{NPh}_{N}>C\cdot SH$ is formed; it crystallises from absolute alcohol in yellow needles, and melts at 208°. The *sodium* salt separates from the alkaline solution in white leaflets, and is decomposed by water.

By Otto Fischer and W. Hofmann.—The *acetyl* derivative of paranitrosophenyl-α-naphthylamine crystallises from wood spirit in lustrous, reddish-yellow leaflets, and melts at 81°. On reducing the base with zinc dust and acetic acid, paramidophenyl-α-naphthylamine is formed; the *acetyl* derivative crystallises in white leaflets, and melts at 192°, the *benzylidene* compound, $NHPh\cdot C_{10}H_6\cdot N{:}CHPh$, separates from absolute alcohol in greenish-yellow crystals, and melts at 109°; and the *orthohydroxybenzylidene* derivative crystallises in long, red needles, and melts at 135°. The *metanitrobenzylidene* compound crystallises in red leaflets, melting at 169°, and the *paranitrobenzylidene* derivative crystallises in very dark red leaflets, and melts at 168°; the *thiocarbamide*, $CS(NH\cdot C_{10}H_6\cdot NHPh)_2$, forms white crystals, and melts at 196°.

α-Naphthaquinonephenyldiimide, $NH{:}C_{10}H_6{:}NPh$, is obtained by agitating a solution of amidophenyl-α-naphthylamine in benzene with mercuric oxide; it forms lustrous, reddish-yellow crystals, and melts at 128—129°. M. O. F.

Piperonylideneacetone. By L. Rousset (*Bull. Soc. Chim.*, 1895, [3], **13**, 348—351).—*Piperonylideneacetone*,

$$CH_2<^{O}_{O}>C_6H_3\cdot CH{:}CHAc,$$

is formed as a yellow precipitate when a solution of piperonal in acetone is shaken with a large excess of cold, 10 per cent., aqueous soda; when purified by recrystallisation from alcohol, it forms minute, yellow, prismatic needles, belonging either to the monoclinic or to the triclinic system, but the product obtained by distillation with steam is colourless; it melts at 96·5°.

The *oxime* is colourless, and melts at about 179°, at the same time decomposing. The *dibromo*-derivative forms colourless crystals, and melts at 76°; it decomposes at 100°.

Piperonylideneacetone is oxidised by chromic acid mixture to piperonylic and acetic acids, and carbonic anhydride. Jn. W.

Reducing Action of Sodium Alkylic Oxides at High Temperatures. By Albin Haller and Jules Minguin (*Compt. rend.*, 1895, **120**, 1105—1106).—Phenyl benzyl ketone, when heated in sealed tubes at 200—210° with sodium ethoxide in presence of excess of alcohol, yields stilbene. Diphenyl ketone, under similar conditions, yields benzhydrol. Anthraquinone, with sodium ethoxide, butyloxide, or amyloxide, yields anthracene. Methyl phenyl ketone seems to yield phenylmethylcarbinol. C. H. B.

Ethereal Salts of Amido-acids. By HEINRICH SALKOWSKI (*Ber.*, 1895, **28**, 1917—1923).—When an attempt is made to crystallise the hydrochloride of paramidophenylacetic acid from boiling alcohol, it is converted into the *hydrochloride* of its *ethylic salt*,

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot COOEt,HCl,$$

which separates in plates, and, on treatment with cold soda solution, yields *ethylic paramidophenylacetate*, melting at 49·5°. The formation of the ethylic salt does not take place at the ordinary temperature, but a similar action occurs on boiling the hydrochloride of the acid with methylic, normal propylic, or amylic alcohol, although, in the case of the first named, the action is far from complete. The hydrochloride of metamidophenylacetic acid behaves in the same manner.

In order to ascertain whether this property is characteristic of aromatic amido-acids in general, the author has examined the behaviour of a number of these, and finds that the hydrochlorides of ortho-, meta-, and paramidobenzoic acids undergo no etherification under these conditions, but that the amidocinnamic and amidohydrocinnamic acids all readily undergo etherification; the results are not altered if the hydrobromide, hydriodide, or nitrate are employed in place of the hydrochloride, but with the sulphate no etherification takes place. It appears, therefore, that aromatic amido-acids in which the carboxyl group is not directly combined with the benzene nucleus undergo etherification by the action of boiling alcohol on their salts with hydrochloric, hydrobromic, hydriodic, or nitric acid, the relative position of the amido-group to the side chain containing the carboxyl having no influence. This conclusion is analogous in many respects to that of V. Meyer and Sudborough (Abstr., 1894, i, 463), who have shown that diortho-substituted benzoic acids do not undergo etherification when treated with methylic alcohol and hydrochloric acid, but that etherification readily takes place in diortho-substituted acids with longer side chains. H. G. C.

Action of Hydrazine Hydrate on Benzylidenecyanhydrin. By ATTILIO PURGOTTI (*Gazzetta*, 1895, **25**, i, 117—121).—On boiling an alcoholic solution of benzylidenecyanhydrin with hydrazine hydrate and distilling off the alcohol, a residue is obtained from which a small proportion of α-toluonitrile may be separated by fractional distillation; no other product was isolated. W. J. P.

Preparation of Thymolphthalide. By PIOTR JAKIMOWICZ (*Ber.*, 1895, **28**, 1876).—The author has obtained thymolphthalide, $C_6H_4<\overset{\text{———}CO}{C(OC_{10}H_{13})_2}>O$, by gently warming powdered thymol (2 mols.) with phthalic chloride (1 mol.). It crystallises in thick, colourless plates, melts at 84—85°, and dissolves in concentrated sulphuric acid, forming a dark red solution. J. J. S.

Methylic Carbonates derived from Polyhydric Phenols. By VICTOR SYNIEWSKI (*Ber.*, 1895, **28**, 1874—1876).—If quinol (1 mol.) intimately mixed with calcined sodium carbonate, is added to a solu-

tion of methylic chloroformate in benzene, and the mixture heated during several hours on the water bath, *methylic quinol dicarbonate*, $C_3H_4(O{\cdot}COOMe)_2$, is formed; this crystallises in long, thin, colourless plates, which melt at 115°.

Methylic resorcinol dicarbonate forms long, white needles, and melts at 44—45°.

In preparing the corresponding catechol and pyrogallol derivatives, calcium carbonate must be substituted for the sodium carbonate.

Methylic catechol dicarbonate crystallises in fine, colourless needles, and melts at 41°.

Methylic pyrogallol tricarbonate, $C_6H_3(O{\cdot}COOMe)_3$, is a thick, yellowish oil.

Methylic orcinol dicarbonate, $C_6H_3Me(O{\cdot}COOMe)_2$, forms long, colourless needles, and melts at 55°. J. J. S.

Eugenol Derivatives. By Ch. Gassmann and Eugen Krafft (*Ber.*, 1895, **28**, 1870—1872).—*Sodium eugenolacetate*,

$$CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COONa\ [= 1:3:4],$$

is obtained when eugenol is heated with sodium hydroxide solution and monochloracetic acid during 20 hours. The *acid* crystallises in colourless needles, melts at 75°, and is readily soluble in hot water, alcohol, acetone, benzene, and light petroleum, but only sparingly in cold water; it is only slightly volatile with steam. When this acid is heated with potassium hydroxide and amylic alcohol during 20 hours. it is converted into *potassium isoeugenolacetate*. *Isoeugenolacetic acid* forms colourless needles, and melts at 92—94°; it cannot be crystallised from water.

When the iso-acid is oxidised with potassium permanganate in alkaline, or, better still, in neutral, solution, the chief products are acetaldehyde and *vanillinacetic acid*,

$$COH{\cdot}C_6H_3(OMe){\cdot}O{\cdot}CH_2{\cdot}COOH\ [= 1:3:4],$$

which is identical with the acid described by Elkan (Abstr., 1887, 259) as vanillinoxyacetic acid. When the acid is treated with phosphorus pentachloride (2 mols.), vanillin, trichloracetic acid, and carbonic anhydride are formed. J. J. S.

Phenylazocarboxylic acid and Tribromophenylazocarboxylic acid. By Oscar Widman (*Ber.*, 1895, **28**, 1925—1931).—E. Fischer has shown (Abstr., 1878, 302) that when phenylsemicarbazide is treated with sodium nitrite in acid solution, it yields a crystalline nitroso-derivative, and that this, on boiling with alkalis, is converted into diazobenzeneimide, carbonic anhydride, and water. The author has reinvestigated this substance, which has the constitution, $NO{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, and melts at 126—127°, with evolution of nitrous fumes. If kept for a long time, it undergoes spontaneous decomposition into *phenylazocarbamide*, $NPh{:}N{\cdot}CO{\cdot}NH_2$, which may, however, be more readily obtained by carefully oxidising phenylsemicarbazide with potassium permanganate or dichromate. It crystallises from water or benzene in long, red needles, melting at 114°,

does not reduce Fehling's solution, but evolves nitrogen on the addition of copper powder to the boiling aqueous solution; it evolves ammonia on warming in alkaline solution, and forms salts of phenylazocarboxylic acid, which are yellow, but have not been obtained pure; on the addition of acids, it decomposes, forming benzene, carbonic anhydride, and nitrogen, together with other products.

Ethylic phenylcarbazinate, NHPh·NH·COOEt, obtained by mixing phenylhydrazine and ethylic chloroformate in ethereal solution, crystallises in long plates, or flat needles; these contain 1 mol. H_2O, which is evolved on heating at 85°; the hydrated compound melts at 79—80°, and the anhydrous compound at 82—83°. The solution in concentrated sulphuric acid is coloured deep red by ferric chloride. When oxidised by potassium permanganate, it yields ethylic phenylazocarboxylate, NPh:N·COOEt, which is a thin, red oil, and is converted into phenylazocarbamide on treatment with concentrated ammonia.

These substances are closely allied to the azodicarbamide derivatives obtained by Thiele (Abstr., 1892, 1429), the additive compounds of diazocyanides and hydrocyanic acid obtained by Gabriel (Abstr., 1880, 41), and further with the substituted diazocyanides recently described by Hantzsch and Schultze (this vol., i, 348) which exist in two modifications, regarded by them as stereoisomerides. Theoretically, the above derivatives are also capable of existing in two stereoisomeric forms, and the author has endeavoured to obtain evidence on this point, employing symmetrical tribromophenylsemicarbazide as the starting point, as this forms more stable derivatives.

Symmetrical *tribromophenylsemicarbazide*,

$$C_6H_2Br_3\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

is readily obtained by the action of potassium cyanate and acetic acid on symmetrical tribromophenylhydrazine, and forms very sparingly soluble needles, melting at 235—236°, with evolution of gas. When oxidised with acetic acid and potassium permanganate, it is converted into the corresponding symmetrical *tribromophenylazocarbamide*, $C_6H_2Br_3\cdot N:N\cdot CO\cdot NH_2$, which crystallises from benzene in long, flat, red needles, and melts and evolves gas at 176°; no definite evidence of the existence of an isomeric compound could, however, be obtained.

Potassium tribromophenylcarboxylate may be obtained by the action of aqueous potash on the carbamide; it crystallises in long, yellow needles, which explode on warming, or when touched with concentrated sulphuric acid. On adding dilute sulphuric acid to the well cooled solution, a yellowish-white precipitate separates, probably consisting of the free tribromophenylazocarboxylic acid, but this decomposes in a few seconds with evolution of gas and formation of tribromobenzene.

During the investigation, the following acetyl derivatives of symmetrical tribromophenylhydrazine were prepared. *β-Acetyltribromophenylhydrazine*, $C_6H_2Br_3\cdot NH\cdot NHAc$, which forms well developed, four-sided prisms, and melts at 188°, and *αβ-diacetyltribromophenylhydrazine*, $C_6H_2Br_3\cdot NH\cdot NAc_2$, crystallising in brittle needles melting at 144—145°. H. G. C.

Sulphur Derivatives of Imidodicarboxylic acid. By EMIL FROMM (*Ber.*, 1895, **28**, 1935—1940).—The imidodicarboxylates described by the author (Abstr., 1893, i, 575, this vol., i, 418, 461), are, with one exception, not acted on by alkyl haloïds in alkaline solution with substitution of the alkyl radicle for the hydrogen of the imido-group. Trithiodibenzylic imidodicarboxylate, however, is acted on under these conditions forming *trithiotribenzylic pseudoimidodicarboxylate*, which crystallises in spherical aggregates of needles melting at 92°. Two formulæ are possible for this substance, namely,

$$C_7H_7N<\begin{matrix}COSC_7H_7\\CSSC_7H_7\end{matrix}, \text{ and } C_7H_7\cdot CO\cdot S\cdot N{:}C(SC_7H_7)_2,$$

as, however, it yields no benzylamine, but considerable quantities of ammonia when distilled with aqueous potash, its constitution must be represented by the second formula. In its formation, the trithiodibenzylic imidodicarboxylate reacts in the tautomeric form,

$$C_7H_7S\cdot CO\cdot N{:}C(SH)\cdot SC_7H_7,$$

and it is probably owing to their incapability of reacting in this form that the other imidodicarboxylates are not affected by benzylic chloride and soda.

When phenylmethylthiobiuret is heated wtth benzylic mercaptan and hydrochloric acid on the water bath, it is converted into *benzylic trithioallophanate*, $C_7H_7S\cdot CS\cdot NH\cdot CS\cdot NH_2$, which forms sulphur-yellow needles and melts at 142—143°. The action of ammonia on this substance was investigated in the hope that the hitherto unknown dithiobiuret would be formed; this is, however, not the case, the products of the action being benzylic mercaptan and ammonium thiocyanate. H. G. C.

Pariodophenylmercapturic acid. By EUGEN BAUMANN and P. SCHMITZ (*Zeit. physiol. Chem.*, 1895, **20**, 586—594).—The acid was obtained from the urine of a dog to which iodobenzene (100 grams) had been administered during about six weeks; the yield was 20—21 per cent. of the iodobenzene employed. The compound crystallises in aggregates of long needles, melts at 152—153°, and decomposes at 190°; the corresponding bromo- and chloro-derivatives melt at 152—153° and 153—154° respectively. It is decomposed by concentrated sulphuric acid, but dissolves without change in alkalis and concentrated hydrochloric acid; the rotatory power $[\alpha]_D = -10{\cdot}4°$ in 2·5 per cent. alcoholic solution. The *silver salt*. $C_{11}H_{11}O_3ISNAg$, is amorphous; the *barium salt* crystallises with $2H_2O$; the *ethylic salt* forms colourless needles melting at 104—105°. All the salts are dextrogyrate, the rotatory power increasing with the concentration, for the sodium salt, $[\alpha]_D = +8°$; $+12{\cdot}7$; $+16{\cdot}7°$ for solutions containing 5·327 grams, 10·654 grams and 21·306 grams per 100 c.c. respectively; the corresponding values for the bromo-acid are + 7°, + 7°, + 9·5° for solutions containing 5·362 grams; 10·724 grams; and 21·448 grams, equivalent to 5, 10, and 20 grams of free acid respectively. When heated with moderately concentrated sulphuric acid, pariodophenylmercapturic acid is resolved into acetic acid and

iodophenylcysteïne, $NH_2{\cdot}CMe(SC_6H_4I){\cdot}COOH$, the *hydrochloride* of which is deposited in feathery transparent crystals; these readily dissociate in contact with water. By the action of potassium cyanate on iodophenylcysteïne, the *uramido-acid*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CMe(SC_6H_4I){\cdot}COOH,$$

is formed, and crystallises in small needles melting at 195—196°. With acetic anhydride, iodophenylcysteïne regenerates the mercapturic acid. When heated with potash, iodophenylmercapturic acid is resolved into ammonia, acetic acid, pyruvic acid and *pariodophenylmercaptan*. The latter crystallises in needles, melts at 85—86°, has a characteristic odour of aniseed, gives yellow precipitates with copper, lead, and silver salts, and is rapidly oxidised by the air to pariodophenylic bisulphide, $C_{12}H_8I_2S_2$; this crystallises in plates, melts at 124°, and gives a dark-blue solution when warmed with sulphuric acid. Both compounds were identical with synthetical preparations obtained from iodobenzenesulphonic acid, proof being thus afforded that the iodine is in the para-position. Pariodophenylmercapturic acid is thus shown to have the formula

$$NHAc{\cdot}CMe(SC_6H_4I){\cdot}COOH.$$ J. B. T.

Synthesis of the Diphenylic Hydrocarbons: Para- and Orthophenyltoluenes. By Giuseppe Oddo and A. Curatolo (*Gazzetta*, 1895, **25**, i, 126—136).—A diazotised mixture of aniline and paratoluidine is slowly added to alcoholic sodium ethoxide, gas is evolved, and, after heating on the water bath in a reflux apparatus, the solution is distilled in a current of steam. The distillate is extracted with ether and the extract evaporated; on fractionally distilling the residue, paraphenyltoluene, C_6H_4PhMe, is obtained as a colourless liquid, which boils at 262—268°, and solidifies in a mixture of ice and salt; it is accompanied by small quantities of benzene, toluene, and diphenyl.

By substituting orthotoluidine for its para-isomeride in the above process, orthophenyltoluene may be prepared; it is an oil which does not solidify in a mixture of ice and salt, boils at 261—264°, and yields orthodiphenylcarboxylic acid on oxidation with chromic acid. It readily takes up bromine, yielding a *tribromo*-derivative, $C_{13}H_9Br_3$, which crystallises in long, white needles melting at 167—169°, and is easily oxidised by chromic mixture; by the aid of this compound, it is shown that a very small proportion of orthophenyltoluene is formed by the action of sodium on a mixture of bromobenzene and orthobromotoluene in ethereal solution. W. J. P.

Action of Hydrazine Hydrate on Benzoïn and on Deoxybenzoïn. By Theodor Curtius and A. Blumer (*J. pr. Chem.*, 1895, [2], **52**, 117—137).—*Benzoïnhydrazine*, $OH{\cdot}CHPh{\cdot}CPh{:}N{\cdot}NH_2$, is prepared by warming a mixture of benzoïn (40 grams) and hydrazine hydrate (11½ grams) on the water bath for four hours, and then setting it aside for eight days. It crystallises in thick, colourless prisms, melts at 75°, and dissolves in alcohol, ether, chloroform, and benzene, but not in water or alkalis. It reduces Fehling's solution and ammo-

niacal silver nitrate; acid converts it into benzoïn and a hydrazine salt; boiling water also decomposes it.

When benzoïnhydrazine is kept at 110° for some hours, and the mass is then extracted with hot alcohol, white needles separate from the alcoholic solution; these have the empirical formula $C_{14}H_{10}N$, melt at 246°, and sublime unchanged; they dissolve in sulphuric acid with a crimson colour and are reprecipitated on dilution; ether and chloroform dissolve them freely, alcohol sparingly, water and alkalis not at all. From the mother liquor of these crystals, bisbenzoylphenylazimethylene (see below) separates, and is followed by a new *compound*, probably $<\begin{matrix}CHPh\cdot NH\cdot CHPh\\ CPh{:}N\text{——}N{:}CPh\end{matrix}>$, which melts at 261°, sublimes unchanged, and dissolves in strong acids without apparent change; ether dissolves it sparingly, alcohol and chloroform easily. The same compounds are formed when an alcoholic solution of benzoïnhydrazine is heated for many days, or when hydrogen chloride is passed into ether which contains benzoïnhydrazine in suspension.

Acetylbenzoïnhydrazine, OH·CHPh·CPh:N·NHAc, crystallises in white needles and melts at 132°. A *monosodium* and a *disodium* derivative of benzoïnhydrazine are described.

Benzylidenebenzoïnazine, OH·CHPh·CPh:N·N:CHPh, obtained by adding benzaldehyde to an alcoholic solution of benzoïnhydrazine, crystallises in white nacreous needles, melts at 133°, and dissolves in ether and alcohol, but not in water. *Orthonitrobenzylidenebenzoïnazine* forms white needles, melts at 195°, and dissolves in hot alcohol and in ether. *Metanitrobenzylidenebenzoïnazine* crystallises in yellow needles, melts at 192°, and dissolves in alcohol and chloroform, sparingly in ether, and not at all in water. *Cuminylbenzoïnazine* crystallises in yellowish, nacreous laminæ, melts at 117°, and dissolves freely in alcohol, ether, and chloroform, but not in water.

Benzoïnketazine, OH·CHPh·CPh:N·N:CPh·CHPh·OH, was obtained by the action of benzoïn on benzoïnhydrazine; it is colourless, and melts at 157°.

Bisbenzoylphenylazimethylene, COPh·CPh:N·N:CPh·COPh, prepared as described above, crystallises in yellow needles, melts at 202°, and dissolves in glacial acetic acid, ether, chloroform, and hot alcohol, but not in hydrochloric acid, caustic soda, or water; it distils unchanged. It is precipitated from its solution in strong sulphuric acid unchanged, unless the solution has been kept, in which case benzile and hydrazine sulphate are produced. Reduction with zinc dust in glacial acetic acid converts bisbenzoylphenylazimethylene into benzyl phenyl ketone and ammonia.

Benzylphenylmethylenehydrazine, $CH_2Ph\cdot CPh{:}N\cdot NH_2$, is prepared by heating benzyl phenyl ketone (5 grams) with hydrazine hydrate (1·3 grams) and a couple of drops of alcohol in a sealed tube at 140° for five hours; it crystallises in white needles, melts at 62°, and dissolves freely in alcohol, ether, and chloroform; it distils unchanged, and reduces ammoniacal silver nitrate and Fehling's solution. This hydrazine is a true secondary hydrazine, undergoing condensation with aldehydes in the cold and with ketones when

warmed. When treated with iodine in alcohol, it is converted into *bisbenzylphenylazimethylene* (*benzylphenylketazine*)

$$CH_2Ph{\cdot}CPh{:}N{\cdot}N{:}CPh{\cdot}CH_2Ph,$$

which crystallises in small, straw-coloured needles, melts at 164°, distils unchanged, and dissolves in ether and chloroform, but not in water. A. G. B.

The Induline Group. By Otto Fischer and Eduard Hepp (*Annalen*, 1895, **286**, 187—247; compare Abstr., 1893, i, 333, and this vol., i, 527).—The system of nomenclature already developed (*loc cit.*) is retained, benzeneindulines, in which the substituent radicle takes up the position R (general formula I) being referred to as *meso*-derivatives.

The most productive source of meso-phenylinduline, $C_{18}H_{13}N_3$, is aposafranine (Abstr., 1893, i, 613). This base is characterised by its green solution in oil of vitriol, the colour of the solution in acid containing the monhydrate or anhydride being brownish-red; the salts form magenta-red solutions in water. The base dissolves readily in methylal, and, on evaporation of the solvent, is deposited as a crystalline crust, having a beautiful, dark green reflex; when dry, it may be heated at 100° without undergoing change, but, on boiling the solution in benzene, a powder separates, forming a brown solution in concentrated sulphuric acid, and dissolving with difficulty in the dilute acid or in acetic acid, yielding reddish-violet solutions. At the same time, a small quantity of meso-phenylinduline is formed, this being most readily obtained by heating aposafranine hydrochloride with aniline in the manner already described (*loc. cit.*). The *nitrate* of meso-phenylinduline crystallises from alcohol in lustrous, green needles; the *platinochloride* forms slender crystals having a dark green reflex, and the *aurochloride* crystallises in lustrous, green needles. The base itself, which has also been called amidoazobenzeneinduline, melts at 203—204°, and not at 215° as previously stated (*ibid.*, 335); the action of a mixture of glacial acetic and hydrochloric acids, during six hours at 160—170°, gives rise to benzeneindone hydrate, whilst treatment with alcoholic barium hydroxide for 10 hours at 140—145° converts it into benzeneindone (Abstr., 1892, 341). *Phenylmesophenylinduline*, $C_{24}H_{17}N_3$, has already been described as the product of the action of aniline on mesophenylinduline, and is most conveniently obtained by heating aposafranine with aniline for an hour at 150—160°; *paratolylmesoparatolylinduline* has been prepared by a similar process, and melts at 227—228°.

Phenylmesoamidophenylinduline (*loc. cit.*) is formed when azophenine (4·5 grams) and paraphenylenediamine hydrochloride (2 grams) are heated with aniline (10 grams) and alcohol (50 grams) for 12 hours at 140°; this process depends on the oxidation of a mixture of paraphenylenediamine and aniline, and the same principle is probably involved in an alternative method, when these bases are heated at 150° with quinonedianil. The base is primary in character, and the *formyl* derivative crystallises in bluish-green leaflets, which transmit red light, and melt at 230°; the *monacetyl* derivative softens

at 150° and melts at 160°, and yields an *acetate* which melts and decomposes at 183°.

Unsymmetrical *hydroxybenzeneindone* is obtained by heating phenylmesoamidophenylinduline with alcoholic barium hydroxide for $3\frac{1}{2}$ hours at 180—200°, and is freed from mesohydroxyphenylinduline by treatment with dilute hydrochloric acid, which precipitates the latter base; the crystalline substance has a bronze lustre, and the solution in concentrated sulphuric acid is brownish-red, becoming orange on dilution. The dilute solution in alkalis is red, and exhibits greenish fluorescence, which is also noticeable in the alcoholic solution. The *hydrochloride* of mesohydroxyphenylinduline, which is formed at the same time, separates from glacial acetic acid on the addition of water in lustrous, green crystals; the solution in concentrated sulphuric acid is green, becoming brownish-red and finally red on dilution, whilst the red, alcoholic solution exhibits feeble, brown fluorescence.

The *benzylidene* derivative of phenylmesoamidophenylinduline crystallises from the dark red, alcoholic solution in small needles, having a green reflex; it melts at 261—262°, and in the finely divided state has electrical properties and transmits red light. The *orthohydroxybenzylidene* compound crystallises in dark brown leaflets transmitting reddish-yellow light.

As already suggested, the mauveïnes and indazines are to be regarded as symmetrical indulines, having the general formula $NH{:}C_6H_3{<}\overset{N}{\underset{NR}{}}{>}C_6H_3{\cdot}NH_2$. In preparing dimethylmauveïne from nitrosodimethylaniline and diphenylmetaphenylenediamine, a *base*, $C_{28}H_{27}N_5$, is obtained; this dissolves in benzene, forming a violet solution, and, on evaporating the solvent, is deposited as a lustrous, green, crystalline powder, which contains benzene and melts at 178°; when this is heated in the vapour of boiling xylene, the benzene is removed, and the substance then melts at 210—212°. The formation of two bases is also observed when nitrosomonomethylaniline, nitrosomonethylaniline, or nitrosodiethylaniline is heated with diphenylmetaphenylenediamine. Thus, *phenylamidophenylmauveïne*,

$$NHPh{\cdot}C_6H_4N{:}C_6H_3{<}\overset{N}{\underset{NPh}{}}{>}C_6H_3{\cdot}NHPh,$$

is formed, together with phenylmauveïne, when nitrosodiphenylamine (28 grams) and diphenylmetaphenylenediamine (26 grams) are heated with 40 per cent. hydrochloric acid (5·5 grams) and alcohol (800 grams) on the water bath, and allowed to remain for 20 hours at the ordinary temperature; the crystals have a bronze lustre, and the substance sinters at 175°, and melts and decomposes at 202°. *Phenylmauveïne*, $NH{:}C_6H_3{<}\overset{N}{\underset{NPh}{}}{>}C_6H_3{\cdot}NHPh$, can be obtained from the mother liquor. The solution of this base in concentrated sulphuric acid is grass green, a greenish-blue coloration being developed when phenylamidophenylmauveïne is dissolved in concentrated sulphuric acid; it is less readily soluble in benzene than the foregoing base, the solution being reddish-violet, and depositing the base in crystals which

contain the solvent. After being dried at 140°, the base melts at 256—257°.

Symmetrical B_2-4-*anilidobenzeneinduline* (mauvindone),

$$C_6H_3O\begin{matrix}<^{N}_{NPh}>\end{matrix}C_6H_3\cdot NHPh$$

(Abstr., 1893, i, 464), dissolves only sparingly in benzene and toluene, but is more readily soluble in alcohol, and is deposited from a mixture of benzene and alcohol as a crystalline powder with bronze lustre; the solution in concentrated sulphuric acid is bluish-violet, becoming red on dilution. When the base is heated with alkalis, or when phenylmauveïne is heated with alcoholic barium hydroxide for 5—10 hours at 180°, symmetrical *hydroxybenzeneindone* is formed, and this is found to be identical with safranol obtained by the action of alcoholic potash on phenosafranine, which is converted first into the symmetrical induline, yielding *amidobenzeneindone*,

$$C_6H_3O\begin{matrix}<^{N}_{NPh}>\end{matrix}C_6H_3\cdot NH_2,$$

on protracted treatment with alcoholic potash. From benzene containing some alcohol, it crystallises in magnificent prisms, having a green lustre; the base is somewhat soluble in water, and the solution in concentrated sulphuric acid is violet, becoming pale brown on dilution. When aposafranine is heated with alcoholic potash for 16 hours, a certain amount of benzeneindone hydrate is formed, together with a blue colouring matter.

According to this method of preparation, safranol contains only one hydroxyl group, although Nietzki and Otto have regarded it as a dihydroxy-derivative; moreover, the ethers contain only one ethyl group and are insoluble in alkalis. The *ethyl ether* crystallises from alcohol in prisms having a bronze lustre; it melts and decomposes at 265°, and dissolves in concentrated sulphuric acid with a reddish-brown coloration, becoming yellow on dilution. The alcoholic solution is red, and exhibits feeble, brown fluorescence. The *methyl ether* melts at 240°.

Mononitrophenylrosinduline is obtained by adding potassium nitrate to a solution of phenylrosinduline in concentrated sulphuric acid and heating the liquid at 50—60°; it crystallises in almost black leaflets with a green reflex, sinters at 250°, and melts at 270°. The solution in concentrated sulphuric acid is green. *Trinitrophenylrosinduline* is formed on adding fuming nitric acid to a solution of phenylrosinduline in glacial acetic acid; it crystallises from nitrobenzene in red leaflets or needles. These nitro-derivatives yield rosindone and nitranilines when heated with glacial acetic acid and concentrated hydrochloric acid for some hours at 180—200°. *Mononitrorosindone* separates from its solution in nitrobenzene in dark red crystals, and from glacial acetic acid in bright red needles; the solution in concentrated sulphuric acid is violet. *Amidorosindone* crystallises from ether in lustrous, dark blue leaflets; it forms two series of salts, one being blue, the other reddish-yellow.

Nt_2-3′-*Hydroxyrosindone*, $C_{22}H_{14}N_2O_2$, is formed when sodium phenylrosindulinesulphonate is heated with 10 per cent. sodium hydroxide (10 parts) at 220°, the *sodium* salt separating in red leaflets as the liquid cools. The compound crystallises from alcohol in prisms having a dark, brownish-green reflex; the alcoholic solution exhibits greenish fluorescence, and the solution in concentrated sulphuric acid is reddish-violet, becoming yellow on dilution.

Nt_2-2′-*Hydroxyrosindone* is obtained by the same method from the corresponding sulphonic acid, forming a *sodium* salt which crystallises in lustrous leaflets, and dissolves in 400 parts of water. The *hydrochloride* crystallises in compact, red prisms having a green reflex, and the alcoholic solution exhibits greenish-yellow fluorescence. Hydroxyrosindone crystallises from alcohol in yellowish-red leaflets; its solution in concentrated sulphuric acid is magenta coloured, in alkalis brownish-yellow, and in alcohol greenish-yellow, exhibiting fluorescence of the same tint.

Symmetrical *anilidophenylinduline* is prepared by gently heating a mixture of nitrosophenyl-α-naphthylamine hydrochloride, and diphenylmetaphenylenediamine dissolved in alcohol; the green liquid soon becomes blue, and is then set aside for 12 hours. The base separates as a bluish-violet powder, and crystallises from benzene in leaflets having a greenish lustre. The *hydrochloride* is deposited from the alcoholic solution as a bluish-violet, crystalline powder. When the salt is heated with glacial acetic acid and concentrated sulphuric acid for nine hours at 200—220°, B_2-4-hydroxyrosindone is formed, this substance being also produced by the action of hydrochloric and glacial acetic acids on amidophenylrosinduline (*ibid.*, 335).

The compound obtained from nitrosodimethylaniline, α-naphthylamine hydrochloride, and aniline, which was regarded as B_1-dimethylisorosinduline (*ibid.*, 336), has, in reality, the constitution

$$NMe_2{\cdot}C_6H_4{\cdot}N{:}C_{10}H_5{\leqslant}\begin{matrix}N\\NPh\end{matrix}{>}C_6H_3{\cdot}NMe_2.$$

This view of its structure receives support from the conversion of the substance into B_2-4-hydroxyrosindone by means of hydrochloric acid at 180°, and also from its formation by the action of nitrosodimethylaniline on β-phenylnaphthylamine, as, from the constitutional formula now put forward, it is seen to be a derivative of β-phenylnaphthylamine. The action of nitrosodimethylaniline on β-phenylnaphthylamine gives rise to an *isomeride* which forms reddish-brown crystals, the solution in alcohol being reddish-violet, and becoming magenta-red when treated with mineral acids; the solution in concentrated sulphuric acid is green, but neither the base nor its salts exhibits fluorescence in solution.

When benzeneazo-α-naphthylamine hydrochloride is heated with phenol for an hour at 120—130°, *rosinduline*, $C_{22}H_{15}N_3$, and "naphthyl red," $C_{26}H_{18}N_4$, are produced (*ibid.*, i, 721). The former is separated by means of the ready solubility of its hydrochloride in dilute alcohol; it crystallises from benzene in aggregates of leaflets and melts at 198—199°. Naphthyl-red is a brownish-red, crystalline

substance, having a green iridescence; it is somewhat soluble in hot water, and absorbs carbonic anhydride from the air. The *hydrochloride* crystallises from dilute alcohol in long, golden needles; the solution in concentrated sulphuric acid is yellowish-green, becoming pink and finally reddish-violet on dilution. Although not very soluble in cold water, the reddish-violet solution exhibits an intense fluorescence resembling that of Magdala red. The *platinochloride* is a brown, crystalline powder.

Nt_2-4-*Amidonaphthindone*, $C_{26}H_{17}N_3O$, is obtained by heating the hydrochloride of naphthyl-red with glacial acetic acid and concentrated hydrochloric acid for nine hours at 190—200°; it crystallises from alcohol in beautiful, green plates. The solutions in alcohol and benzene exhibit fiery-red fluorescence, and the solution in concentrated sulphuric acid is blue by reflected, red by transmitted light, becoming brownish-yellow, and, finally, red on dilution. The *hydrochloride* crystallises in needles with a bronze lustre. The Nt_2-4-hydroxynaphthindone, obtained by decomposing anilidophenylnaphthinduline, is also formed when the hydrochloride of naphthyl-red or amidonaphthindone is heated with acetic and hydrochloric acids for about 20 hours at 200—220°.

When commercial Magdala red is covered with hot benzene, heated with alcoholic potash for 15 minutes, filtered, and again boiled with benzene, it is separated into two bases, one of which, $C_{30}H_{19}N_3$, remains dissolved in the benzene, whilst the residue consists of the amido-derivative, $C_{30}H_{20}N_4$. The solution of the former in concentrated sulphuric acid is blue, but the addition of a few drops of water causes the liquid to appear yellowish-green by transmitted light and pink by reflected light. The second base forms a yellowish-green solution in concentrated sulphuric acid, the liquid becoming brownish-pink and ultimately red on dilution, whilst both bases exhibit fluorescence in alcoholic solution. The base $C_{30}H_{19}N_3$, symmetrical *meso-α-naphthylnaphthinduline*, crystallises from benzene in brownish-red leaflets; when heated with glacial acetic and concentrated hydrochloric acids for 15 hours at 220°, it yields *meso-naphthylnaphthindone*, $C_{10}H_5O\langle\overset{N}{\underset{N(C_{10}H_7)}{\text{———}}}\rangle C_{10}H_6$, which separates from alcohol in prismatic crystals, and dissolves in concentrated sulphuric acid with a bluish-green coloration.

Magdala red is obtained from the residue left by the commercial substance after treatment with alcoholic potash and benzene; when this is dissolved in alcohol with the addition of sulphuric acid, the sulphate is obtained in crystals with a bronze reflex. The *base*, $C_{30}H_{20}N_4$, crystallises in small prisms with a green reflex; they contain ether, but this is completely removed in the vapour of boiling xylene; it dissolves sparingly in benzene and ether, but is more readily soluble in methylal. The aqueous and alcoholic solutions do not exhibit fluorescence, but they absorb carbonic anhydride from the air, developing a vivid red fluorescence which disappears on the addition of alkalis. When the alcoholic solution of the sulphate is treated with sulphuric acid and sodium nitrite, the base, $C_{30}H_{19}N_3$, is formed. When heated with glacial acetic and concentrated hydro-

chloric acids for 20 hours at 200—210°, *amido-meso-naphthylnaphthindone* is formed, and crystallises in needles; the solution of this in concentrated sulphuric acid is blue by reflected, red by transmitted light, and, when diluted, becomes violet, and ultimately red. *Hydroxy-meso-naphthylnaphthindone*, $C_{30}H_{18}N_2O_2$, formed at the same time, separates from alcohol in prismatic crystals having a green lustre; its solution in concentrated sulphuric acid is blue, becoming first carmine, and then yellowish-red on dilution. The *hydrochloride* forms red crystals with a green reflex; the alcoholic solution is yellowish-red, and when dilute exhibits a green fluorescence.

The paper concludes with a table in which the various indones investigated by the authors are collected, together with their principal colour reactions. M. O. F.

Naphthazarin. By Theodor Zincke and M. Schmidt (*Annalen*, 1895, **286**, 27—57; compare this vol., i, 150).—The *diacetyl* derivative of naphthazarin crystallises from hot, glacial acetic acid in lustrous, golden-yellow needles, and melts at 189°; it dissolves in concentrated sulphuric acid with development of a red coloration, and is slowly hydrolysed by alkalis.

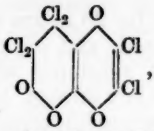
1 : 4 : 1′ : 2′-*Tetrahydroxynaphthalene* is obtained by reducing naphthazarin, suspended in alcohol, with stannous chloride and hydrochloric acid; it crystallises from alcohol in yellow needles, and melts and becomes red at 154°. Very dilute solutions in common solvents exhibit a greenish fluorescence, and the aqueous solution becomes red on exposure to air; the solution in concentrated sulphuric acid is greenish-yellow. The tetracetyl derivative has been already obtained (*loc. cit.*). Tetrahydroxynaphthalene rapidly undergoes oxidation when an alkaline solution is exposed to air, treatment with aqueous sodium hydroxide giving rise to a green salt, which gradually yields a blue solution, from which the sodium derivative of naphthazarin separates in coppery leaflets. Attempts to convert tetrahydroxynaphthalene into a diquinone were unsuccessful, the substance being indifferent towards nitrous acid, atmospheric oxygen, and nitric acid, whilst ferric chloride oxidises it to naphthazarin.

The *dichlorinated* additive compound of naphthazarin

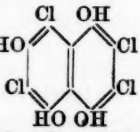
$$[O : (HCl)_2 : O = 1 : 2 : 3 : 4],$$

is prepared by the action of dry chlorine on naphthazarin suspended in cold chloroform; it crystallises in dark-yellow, compact prisms, and decomposes at 220°. When treated with boiling alcohol, 1 mol. HCl is eliminated, and alkalis and alkali carbonates convert it into the blue sodium derivative of monochloronaphthazarin.

Monochloronaphthazarin is obtained by dissolving the dichlorinated additive compound in boiling glacial acetic acid, and heating on the water bath with sodium acetate dissolved in the minimum quantity of water; it crystallises from hot glacial acetic acid in greenish-black needles having a metallic lustre, and melts at 176°. The *diacetyl* derivative crystallises from acetic anhydride in golden-yellow needles, and melts at 192°; it is formed when chlorine acts on the diacetyl derivative of naphthazarin.

Hexachlorotetraketohexahydronaphthalene,  , is prepared by suspending monochloronaphthazarin in glacial acetic acid, saturating the liquid with chlorine, and vigorously agitating it in a closed vessel; it crystallises from benzene in small, pale yellow needles, and from glacial acetic acid in prismatic crystals. It dissolves in hot, fuming nitric acid, from which it separates in yellow crystals; the solution in concentrated sulphuric acid is red.

Tetrachloronaphthazarin is obtained from the foregoing compound by reducing it in hot glacial acetic acid solution with stannous chloride; it is also formed when the hexachloro-derivative is heated with hydrochloric acid at 160° for 10—12 hours, dichloromaleïc acid being produced at the same time. It crystallises from glacial acetic acid in dark red, lustrous plates, and melts at 244°; the salts are deep blue, and dissolve with difficulty in water and alcohol. The compound is indifferent towards alkalis, this behaviour being probably due to the sparing solubility of the alkali salts; these, however, yield naphthazarin very easily when a solution in alcohol or glacial acetic acid is heated with zinc dust. The *acetyl* derivative crystallises from acetic anhydride in golden-yellow needles, and melts at 244°. *Anilidotrichloronaphthazarin* is formed when a solution of the tetrachloro-derivative in glacial acetic acid is boiled with aniline; it crystallises from the acid in brown needles, and melts at 224°. The alkali salts are blue, and the solution in concentrated sulphuric acid is blue, becoming red when heated. The action of chlorine on tetrachloronaphthazarin, dissolved in glacial acetic acid, converts it into the hexachloro-derivative already described; the same effect is produced by bleaching powder.

Tetrachlorotetrahydroxynaphthalene,  , is obtained by the action of stannous chloride on the hexachloro-derivative and tetrachloronaphthazarin; the product is separated as rapidly as possible, and excess of the reducing agent must be avoided.

Solutions of the compound in alkalis are green, the surface of the liquid rapidly becoming coated with a blue, coppery oxidation product. The *tetracetyl* derivative crystallises from acetic anhydride in slender, colourless needles, and melts at 250°.

Tetrachlorotetraketotetrahydronaphthalene is formed when the hexachloro-derivative is cautiously melted, chlorine being evolved. It sublimes when strongly heated, and crystallises in lustrous, yellow leaflets resembling mosaic gold in appearance; common solvents and fuming nitric acid dissolve it with difficulty. Reduction in glacial acetic acid with stannous chloride gives rise to tetrachloronaphthazarin, tetrachlorotetrahydroxynaphthalene being formed when excess of the reducing agent is employed; tetrachloronaphthazarin is also

formed by the action of hot hydrochloric acid. The quinone dissolves in hot quinoline or phenol, giving rise to red compounds. Orthophenylenediamine unites with it, forming an *eurhodole* which is isomeric with the similar compound obtained from tetrachloronaphthazarin, the alcoholic solution being blue, and the ammonium salt sparingly soluble. Aniline converts the quinone into the *dianilido*-derivative, which crystallises from glacial acetic acid in needles having a metallic lustre; the solution in aqueous soda is violet. Concentrated hydrochloric acid at 150° removes one aniline group, which appears to be replaced by an atom of chlorine.

The *eurhodole* obtained from tetrachloronaphthazarin by the action of orthophenylenediamine crystallises in greenish-brown leaflets and needles exhibiting a metallic lustre; it does not melt below 250°, and dissolves with difficulty in common solvents. The *sodium* salt is violet, and dissolves sparingly in alkalis, the solution in alcohol being blue. The *triacetyl* derivative crystallises in yellowish, microscopic prisms, and does not melt below 250°. Another *acetyl* derivative is obtained by boiling the alcoholic solution of diacetyltetrachloronaphthazarin with orthophenylenediamine; it yields the triacetyl derivative when treated with boiling acetic anhydride.

In order to compare the properties of tetrachloronaphthazarin with the behaviour of α-naphthaquinone derivatives towards orthophenylenediamine, the following compounds have been prepared.

αβ-Dichloronaphthaphenazine, $\begin{matrix}CCl\cdot C_6H_4\cdot C{:}N\\ \|\\ CCl\text{——}C{:}N\end{matrix}>C_6H_4$, is obtained by adding orthophenylenediamine to a hot solution of dichloro-β-naphthaquinone in glacial acetic acid; it crystallises in slender, yellow needles, and melts at 202°.

αβ-Hydroxychloronaphthaphenazine (*β-chloronaphtheurhodole*),

$$\begin{matrix}C(OH)\cdot C_6H_4\cdot C{:}N\\ \|\\ CCl\text{——}C{:}N\end{matrix}>C_6H_4,$$

is prepared by the action of the base on dichloro-α-naphthaquinone and hydroxychloro-α-naphthaquinone; it crystallises in brownish-red needles which exhibit a metallic lustre. The solution in hot, aqueous soda is red; dilute aqueous alkali dissolves it when cold, further addition of soda causing separation of the sodium derivative in yellowish-red leaflets and needles having a greenish lustre. Nitric acid (sp. gr. 1·4) oxidises the eurhodole to *diketonaphthaphenazine*,

$$\begin{matrix}CO\cdot C_6H_4\cdot C{:}N\\ |\\ CO\text{——}C{:}N\end{matrix}>C_6H_4$$

(following abstract). M. O. F.

αα-Diketotetrahydronaphthalene Oxide. By Theodor Zincke and P. Wiegand (*Annalen*, 1895, **286**, 58—89; compare **Abstr.**, 1893, i, 220).—Diketotetrahydronaphthalene oxide combines readily with bases, the compounds obtained by the action of aniline having already been described (*loc. cit.*).

β-Naphthylamidohydroxydiketotetrahydronaphthalene,

$$C_6H_4<\begin{matrix}CO\\CO\cdot CH\cdot NH\cdot C_{10}H_7(\beta)\end{matrix}\begin{matrix}CH\cdot OH\\|\\CH\end{matrix}$$

crystallises in needles with a golden lustre; when heated alone, or when treated with boiling glacial acetic acid, it is converted into *β-naphthylamidohydroxy-α-naphthaquinone*, which crystallises in dark blue leaflets, and melts at 178°.

Paratoluidohydroxy-α-naphthaquinone crystallises in deep blue, lustrous leaflets, and melts at 188°; the odour of isocyanide becomes perceptible on dissolving it in aqueous alkali. The *ortho*-derivative melts at 172°.

α-Naphthylamidohydroxy-α-naphthaquinone crystallises from glacial acetic acid in bluish-black leaflets, and melts at 174°; bromine converts it into the *tetrabromo*-derivative melting at 114°; a small quantity of isonaphthazarin is formed at the same time.

When an alcoholic solution of diketotetrahydronaphthalene oxide is heated on the water bath with orthophenylenediamine, a mixture of three products is obtained. The *compound* $\begin{matrix}CO\cdot C_6H_4\cdot C=N-\\|\\CH(OH)\cdot CH\cdot NH\end{matrix}>C_6H_4$ separates from the liquid in brownish-red needles after a few hours; at 150° it becomes blue and decomposes, yielding *αβ-dihydroxynaphthaphenazine* (*αβ-hydroxynaphtheurhodole*),

$$\begin{matrix}C(OH)\cdot C_6H_4\cdot C:N\\||\\C(OH)\text{———}C:N\end{matrix}>C_6H_4,$$

a deep blue, crystalline powder which melts at 241°. This substance is formed when an alcoholic solution of diketotetrahydronaphthalene oxide is heated with orthophenylenediamine for half an hour, and can also be prepared from the foregoing compound by treatment with boiling glacial acetic acid, and by the action of aqueous soda or concentrated sulphuric acid; the sodium derivative is green and the sulphate red. The *diacetyl* derivative crystallises in white, lustrous needles, and melts at 208°, a red *monacetyl* derivative being produced when the action of boiling glacial acetic acid is interrupted before the formation of the diacetyl compound. *αβ*-Dihydroxynaphthaphenazine is converted into *αβ*-naphthaphenazine by cautiously heating it with zinc dust in an atmosphere of hydrogen.

αβ-Diketonaphthaphenazine (*naphthaphenazinequinone*),

$$\begin{matrix}CO\cdot C_6H_4\cdot C:N\\|\\CO\text{———}C:N\end{matrix}>C_6H_4$$

is prepared by oxidising dihydroxynaphthaphenazine in glacial acetic acid solution with nitric acid of sp. gr. 1·4; it crystallises in golden-yellow needles, and melts and decomposes at 265°. On reducing it with stannous chloride, the dihydroxy-derivative is regenerated. The *monoxime* crystallises in yellowish-green needles, and melts and decomposes at 219°.

Naphthadiphenazine, $C_6H_4<\begin{matrix}N:C\cdot C_6H_4\cdot C:N\\|\\N:C\text{———}C:N\end{matrix}>C_6H_4$, is the third pro-

duct of the action of orthophenylenediamine on diketotetrahydronaphthalene oxide; it crystallises from glacial acetic acid in slender, white needles, and does not melt below 275°. Mineral acids yield yellow or red salts which are decomposed by water and on exposure to air.

Benzeneazo-β-naphthaquinol (1 : 3 : 4-*benzeneazodihydroxynaphthalene*), $\begin{matrix}C(OH)\cdot C_6H_4\cdot C:N\cdot NPh\\ \|\qquad\qquad\|\\ C(OH)\text{——}CH\end{matrix}$ or $\begin{matrix}CO\cdot C_6H_4\cdot C:N\cdot NHPh\\ |\qquad\qquad|\\ C(OH)=CH\end{matrix}$, is obtained by treating a solution of diketotetrahydronaphthalene oxide in hot, glacial acetic acid with phenylhydrazine in the same solvent; it is also formed on adding the theoretical quantity of diazobenzene chloride to a solution of β-naphthaquinol in alcohol. The substance is dark red; it melts and froths at 214°. The solution in alkalis is blue, rapidly becoming brownish-red, whilst concentrated sulphuric acid dissolves it, developing a deep blue coloration. The *hydrochloride* separates from the blue solution in lustrous, green needles, which closely resemble magenta; it is rapidly decomposed by alcohol, and less easily by water, undergoing but slight change on exposure to air. The *monacetyl* derivative crystallises from hot benzene in red, lustrous needles, and melts at 133°; it is insoluble in cold aqueous alkali, undergoing hydrolysis when heated, this result being also produced by hydrochloric acid. The *diacetyl* derivative is formed when sodium acetate is employed; it crystallises from hot alcohol in orange plates, and melts at 153°. It is easily reduced in alcoholic solution by treating it with zinc dust and glacial acetic acid, the *diacetyl* derivative of benzenehydrazo-β-naphthaquinol being formed; this crystallises in colourless needles, and melts at 178°. It is insoluble in aqueous alkalis, but is converted into benzeneazo-β-naphthaquinol by alcoholic potash. When benzeneazo-β-naphthaquinol is reduced, in alcoholic solution, with zinc dust and glacial acetic acid, it is resolved into aniline and amidodihydroxynaphthalene, the latter being immediately oxidised to hydroxyimidonaphthol, $\begin{matrix}CO\cdot C_6H_4\cdot C:NH\\ |\qquad\qquad|\\ C(OH):CH\end{matrix}$.

Benzeneazo-β-naphthaquinone (1 : 3 : 4-*benzeneazodiketodihydronaphthalene*), $\begin{matrix}CO\cdot C_6H_4\cdot C:N:NPh\\ |\qquad\qquad\|\\ CO\text{——}CH\end{matrix}$, is obtained by allowing an alkaline solution of benzeneazo-β-naphthaquinol in alcohol to remain in an atmosphere of oxygen; the deep blue liquid becomes brown, and the product separates in long, yellow needles. When recrystallised from ether, it melts and evolves gas at 250°. The quinol is regenerated when the alcoholic solution is heated with alkali.

The phenylhydrazone of hydroxynaphthaquinone has been already investigated by Zincke and Thelen, and more recently by Kostanecki; the monacetyl and diacetyl derivatives melt at 173° and 123° respectively. On reducing the diacetyl derivative in alcoholic solution with zinc dust and glacial acetic acid, 1 : 2 : 4-*amidodihydroxynaphthalene* is produced, forming aggregates of colourless crystals; it becomes violet at 130°, and melts to a blue liquid at 162°. It becomes blue on exposure to air, and the solutions in common solvents rapidly

acquire the same colour. The *hydrochloride* crystallises in nacreous leaflets, and forms a green solution in alkalis, ammonia being evolved; on exposure to air, the solution becomes brownish-red, and yields hydroxynaphthaquinone when treated with acids. Acetanilide is a product of the reduction of the diacetyl derivative, whilst aniline is formed, together with amidodihydroxynaphthalene, when the monacetyl derivative is reduced. M. O. F.

Azo Colouring Matters. By EUGEN BAMBERGER and FRANZ MEIMBERG (*Ber.*, 1895, **28**, 1887—1897).—Bamberger's statement (this vol., i, 351) that normal and iso-diazo-compounds yield identical products, is now shown to be true for the products obtained by the action of methylaniline and of ethylaniline on normal and iso-paranitrodiazobenzene.

The authors confirm Hantzsch's statement (this vol., i, 418) that the two isomeric paranitrophenylazo-α-naphthols, obtained by treating paranitrodiazobenzene hydrate with α-naphthol, are position isomerides, being respectively para- and ortho-derivatives of naphthalene.

The following new compounds are described.

Orthonitrophenylparazo-α-naphthol, $OH^{(1)}\cdot C_{10}H_6^{(4,2)}\cdot N_2\cdot C_6H_4^{(1)}\cdot NO_2$, crystallises in dark red needles, which have a bronzy lustre. It decomposes and melts at 244—245°, and is readily soluble in hot xylene and amylic alcohol. When reduced, and then treated with ferric chloride, it gives α-naphthaquinone.

Orthonitrophenylorthazo-α-naphthol, $OH^{(1)}\cdot C_{10}H_6^{(2,2)}\cdot N_2\cdot C_6H_4^{(1)}\cdot NO_2$, is formed, together with the above para-compound, when orthonitrodiazobenzene methyl ether is treated with α-naphthol. It crystallises in brownish-red, glistening needles, melts at 215—216°, and is soluble in concentrated sulphuric acid. It does not yield α-naphthaquinone. Both the ortho-compound and the para-compound are soluble in aqueous alkalis.

Paranitrophenylazodiethylorthotoluidine, $NO_2\cdot C_6H_4^{(1)}\cdot N_2\cdot C_6H_3^{(2)}Me\cdot NEt_2$, forms dark orange-red needles, which have a brilliant lustre, and melt at 107·5—108°. Diethylorthotoluidine, however, gives no dye with paranitroisodiazobenzene.

When paranitrophenylazomethylaniline, dissolved in acetic acid, is added to α-naphthylamine and the mixture is allowed to remain, Meldola's paranitrophenylazo-α-naphthylamine (m. p. 251—252°) separates. α- and β-naphthol are also capable of replacing the aniline group from both paranitrophenylazo-methylaniline and -ethylaniline.

It is also shown that when diazobenzene chloride reacts with alkaline α-naphthol, 33 per cent. of bisphenylazo-α-naphthol is formed; this fact has been overlooked by previous investigators. The compound melts at 190—191°, whereas Krohn (Abstr., 1889, 152) gives 183° as the melting point.

Bisparatolylazo-α-naphthol is formed, together with paratolylazo-α-naphthol, by the action of diazotoluene chloride on an alkaline

solution of α-naphthol. It is insoluble in alkalis, and crystallises in dark violet needles which melt at 205—206°.

Bisparabromophenylazo-α-naphthol, $OH{\cdot}C_{10}H_5(N_2{\cdot}C_6H_4Br)_2$, crystallises in green, glistening needles, which melt at 233—235°. It is sparingly soluble in alcohol, ether, and chloroform, but readily in hot benzene or toluene.

According to the authors, *parabromophenylazo-α-naphthol* crystallises in dark brown needles with a greenish iridescence, and melts at 237—238°, and not at 185° or 195—196°, as Margary (Abstr., 1885, 546) states. J. J. S.

Naphthylindoxazen. By R. J. Knoll and Paul Cohn (*Ber.*, 1895, **28**, 1872—1873).—The *oxime* of orthobromophenyl naphthyl ketone (this vol., i, 477) is obtained when an alcoholic solution of the ketone is heated for 196 hours with an excess of hydroxylamine hydrochloride and a few drops of hydrochloric acid in a soda-water bottle; the yield is not good, as a considerable portion of the ketone remains unaltered. The oxime, which crystallises in small needles, melts at 165°, and is only sparingly soluble in alcohol or light petroleum, but readily in ethylic acetate. It is not soluble in alkalis, and does not reduce Fehling's solution. When the oxime is heated with alcoholic potash, *naphthylindoxazen*, $C_6H_4<\begin{matrix}C(C_{10}H_7)\\ \text{—}O\text{—}\end{matrix}>N$, is formed; this crystallises in small needles, which melt sharply at 92—93°. J. J. S.

Terpenes and Ethereal Oils. By Otto Wallach (*Annalen*, 1895, **286**, 90—118; compare Abstr., 1894, i, 46, also Semmler, *ibid.*, 339).

By Otto Wallach and O. Scharfenberg.—The authors enumerate reasons for regarding thujone, tanacetone, and salvone as chemically identical, and attribute the difference in their physical properties to admixture with foreign substances. For the purposes of this investigation, thujone has been prepared from oils of thuja, tansy, wormwood, and sage; the ethereal oil of *Artemisia Barrelieni* is also a profitable source of the ketone. Three isomeric thujonoximes have been prepared, and the respective amines obtained on reduction are found to be individual substances.

Thujonoxime, melting at 90°, is obtained by treating the isomeric oxime (m. p. 54—55°) with phosphorus pentachloride (*loc. cit.*); it crystallises from light petroleum in large, transparent, monoclinic prisms; $a : b : c = 1{\cdot}285 : 1 : 1{\cdot}377$, $\beta = 116° 28'$. The alcoholic solution is feebly dextrorotatory. Unlike the isomerides, the oxime is not volatile in an atmosphere of steam. When thujonoxime, melting at 54—55°, is dissolved in concentrated sulphuric acid maintained at a temperature below 50—60°, it is converted into an optically inactive *isomeride*, which crystallises from methylic alcohol in long needles and melts at 119—120°; it dissolves readily in water, and is volatile in an atmosphere of steam, slowly becoming hydrolysed when treated with boiling dilute acids.

Thujonamine, obtained by reducing with sodium and alcohol the oxime melting at 54—55°, boils at 195°, has a sp. gr. of 0·8735 and a refractive power $[n]_D = 1{\cdot}4608$ at 20°, being identical with tanacetyl-

amine obtained by reducing tanacetoxime (Semmler, Abstr., 1893, i, 107). It absorbs carbonic anhydride with great readiness, forming the *carbonate*, which melts at 106—107°; the *nitrate* and *hydrochloride* melt at 167—168° and 260—261° respectively. The *phenylcarbamide* crystallises in white prisms and melts at 120°.

The *isomeride* obtained from the oxime melting at 90° boils at 193°, and has a sp. gr. of 0·875 and a refractive power $[n]_D = 1·4625$ at 20°: it absorbs carbonic anhydride slowly. The *nitrate* and *hydrochloride* melt at 124° and 216° respectively, and the *phenylcarbamide* melts at 110°.

The *isomeride* (*isothujonamine*) obtained from the oxime melting at 119—120°, boils at 200—201°, and has a sp. gr. of 0·865 and a refractive power $[n]_D = 1·468$ at 20°; it absorbs carbonic anhydride very feebly. The *nitrate* and *hydrochloride* melt at 163° and 180—181° respectively; the *carbamide*, $NH_2·CO·NH·C_{10}H_{17}$, melts at 158—159°, the *phenylcarbamide* crystallises in white needles and melts at 178°, and the *phenylthiocarbamide* crystallises from methylic alcohol in needles and melts at 152—153°.

Thujene (Abstr., 1893, i, 106), obtained by distilling the hydrochloride of thujonamine (from thujonoxime, m. p. 54—55°), is identical with tanacetene prepared by a similar method from tanacetylamine (Semmler, *loc. cit.*). Isothujonamine hydrochloride, when submitted to dry distillation, also yields thujene, which boils at 170—172°, has a sp. gr. of 0·836 and a refractive index $[n]_D = 1·47145$ at 22°; the identity of this hydrocarbon with thujene obtained from the sources already mentioned has not, however, yet been established. Thujene contains two ethylenic linkings, and differs from all other terpenes in developing an intense, red coloration when a drop of concentrated sulphuric acid is added to its solution in glacial acetic acid.

Isothujone, $C_{10}H_{16}O$, is obtained by heating thujone with a mixture of concentrated sulphuric acid and water (2 parts) for 8—10 hours in a reflux apparatus, the product being subsequently carried over in a current of steam. The points of difference between thujone, isothujone, and carvotanacetone (Semmler, Abstr., 1894, i, 339) are collected in the following table.

	B. p.	Sp. gr.	$[n]_D$.	M.
Thujone	200—201°	0·9175	1·45109	45·20
Isothujone	230—231	0·9285	1·48227	46·69
Carvotanacetone ..	228°	0·9373	1·4835	46·96

Isothujone immediately reduces a cold solution of potassium permanganate; the oxime melts at 119—120°, being identical with the oxime obtained by treating thujonoxime (m. p. 54—55°) with concentrated sulphuric acid; this oxime is invariably obtained from isothujone prepared from oils of thuja, tansy, wormwood, and sage. The ready conversion of thujone into isothujone by means of sulphuric acid suggests a method of separating lævo-fenchone from thujone, as the boiling point of the former is considerably below that of isothujone.

Dihydroisothujole or *thujamenthole*, $C_{10}H_{20}O$, is obtained by reducing

isothujole with alcohol and sodium; it is a viscous liquid, having the odour of terpineol. It boils at 211—212°, has a sp. gr. of 0·9015 and a refractive power $[n]_D = 1·46306$ at 20°.

Thujamenthone, $C_{10}H_{18}O$, is obtained by oxidising the foregoing alcohol in glacial acetic acid solution with chromic anhydride; it boils at 208—211°, has a sp. gr. of 0·897, and a refractive power $[n]_D = 1·4541$ at 20°. The ketone is isomeric with menthone; it is optically inactive, and has the odour of methone. The oxime melts at 95°, and the *semicarbazide* derivative crystallises in needles and melts at 178°.

Whilst endeavouring to identify thujamenthole and thujamenthone with an alcohol and ketone already known, it was found that tetrahydrocarveol and dihydrocarvotanacetol are identical, but differ from thujamenthole, whilst tetrahydrocarvone is identical with dihydrocarvotanacetone and differs from dihydroisothujole.

When thujone is heated in acetic acid solution with ferric chloride, carvacrol is formed, and the same compound is produced, together with carvotanacetone, when thujone is heated alone at a high temperature.

By Otto Wallach and James T. Conroy (Abstr., 1893, i, 598).—When tribromothujone is treated with sodium and methylic alcohol, it yields the *compound* $OH·C_{10}H_{11}Br·OMe$, which forms colourless crystals and melts at 156—157°; it is phenolic in character, forming a nitro-derivative, and the acetyl compound crystallises from methylic alcohol, and melts at 63—64°. The *dimethyl ether*, which melts at 42—43°, is insoluble in alkali, and yields a nitro-derivative by the action of strong nitric acid. The *compound*, $OH·C_{10}H_{11}Br·OEt$, is formed when tribromothujone is dissolved in ethylic alcohol and treated with sodium; it melts at 144—145°, and resembles the methylic compound in general behaviour. An attempt was made to determine the relative position of the oxygen atoms in these compounds. Tribromothujone was dissolved in glacial acetic acid, and heated on the water bath with sodium acetate; on removing the acetic acid, acidifying, and extracting with ether, a product was obtained, which, when oxidised with ferric chloride, yielded a yellow oil having a pronounced odour of quinone. It is, therefore, probable that the hydroxyl groups are in the para-position, and the authors regard the methylic compound (m. p. 156—157°) as having the constitution $CPr\begin{matrix}<\\>\end{matrix}\begin{matrix}CH—C(OH)\\C(OMe)·CBr\end{matrix}\begin{matrix}>\\<\end{matrix}CMe$.

M. O. F.

Terpenes and Ethereal Oils. Brominated Derivatives of the Carvone Series. By O. Wallach (*Annalen*, 1895, **286**, 119—243).—Racemic *carvone tribromide*, $C_{10}H_{14}O,HBr,Br_2$, is obtained by dissolving a mixture of equal quantities of *d*- and *l*-carvone in glacial acetic acid saturated with hydrogen bromide, and having cooled the liquid, adding a solution of bromine in glacial acetic acid; it separates from ethylic acetate in magnificent, monoclinic crystals, and melts at 74—76°. Lævo- and dextro-carvone tetrabromides melt at 120—122°; the racemic tetrabromide melts at 107—109° (compare Abstr., 1894, i, 538). By the further action of bromine on the liquid from which

the tetrabromides are removed, the *α-pentabromide* is formed; the active modifications melt and decompose at 142—143°, and the racemic at 124—126°, the latter being obtained by mixing the lævo- and dextro-pentabromides in equal proportion, and also by the action of bromine on the racemic tetrabromide (m. p. 107—109°). On bromination, dextro-carvone tetrabromide yields the *β-pentabromide*, which is dextro-rotatory, and melts at 86—87°; the derivative from lævo-carvone tetrabromide has the same melting point, and the racemic *β*-pentabromide melts at 96—98°. When the carvone bromides are reduced with zinc dust and glacial acetic acid, carvone is regenerated; carvone tetrabromide dissolves in fuming nitric acid, undergoing moderate oxidation when the solution is heated, and yielding a nitrogenous acid, which is decomposed by alkalis with formation of nitrous acid.

On submitting a solution of racemic carvone tribromide in ethylic or amylic alcohol to the action of a current of dry ammonia, an unstable *base* is formed, of which the salts in aqueous solution yield crystals of a *compound* having the composition $C_{10}H_{14}O_2$; it separates from alcohol in well-defined crystals, melts at 69—70°, and boils at 123° under a pressure of 10 mm. The substance is insoluble in boiling aqueous soda; it is unsaturated, and the *dibromide* melts at 94—96°.

Dihydrocarvone tribromide is obtained by the action of bromine on the *d*- or *l*-dibromide; it melts at 88—89°, and the racemic modification at 65°.

The ketonic compound, $C_{10}H_{16}O$, obtained by heating trihydroxyhydrocymene with dilute sulphuric acid (Abstr., 1894, i, 44), the author calls *carvenone;* on bromination, it yields racemic dihydrocarvone dibromide. The author has already shown (this vol., i, 59) that terpineol may be converted into carvone, and the formation of carvenone from an oxidation product of terpineol affords a means of transforming the alcohol into dihydrocarvone. When dihydrocarvone is heated with dilute sulphuric acid in a reflux apparatus for 10 hours, carvenone is formed, and the production of this substance when trihydroxyhydrocymene is heated with dilute acid depends on the intermediate formation of dihydrocarvone. The abnormal refractive power of carvenone and isothujone has as yet received no explanation, the properties of the substances leaving no doubt as to their ketonic character. Carvacrol is produced when dihydrocarvone and carvenone are oxidised with ferric chloride.

The author discusses the conditions affecting the formation of a racemic compound on mixing *d*- and *l*-modifications; it is found that such combination is almost invariably accompanied by contraction. In connection with this subject, the following crystallographic information has been supplied. Inactive carvone dibromide crystallises in the triclinic system, $a : b : c = 0{\cdot}5057 : 1 : 0{\cdot}5492$; $\alpha = 90° 16'$, $\beta = 107° 18'$, $\gamma = 76° 50'$. The crystals of *i*-carvone tribromide are monoclinic, $a : b : c = 0{\cdot}7154 : 1 : 0{\cdot}7459$; $\beta = 98° 58'$. Dextro- and lævo-carvone tribromides form rhombic hemihedral crystals; $a : b : c = 0{\cdot}4729 : 1 : 0{\cdot}7939$. The *d*- and *l*-carvone tetrabromides also form rhombic hemihedral crystals; $a : b : c = 0{\cdot}7078 : 1 : 0{\cdot}8704$. The inactive

tetrabromide forms monoclinic crystals; $a : b : c = 0{\cdot}7091 : 1 : 0{\cdot}4605$; $\beta = 100° 32' 45''$. The *d*- and *l*-carvone tetrabromides form monoclinic hemimorphic crystals; $a : b : c = 0{\cdot}7842 : 1 : 0{\cdot}6006$; $\beta = 98° 6'$.

M. O. F.

Essence of Cannabis Indica. By G. Vignolo (*Gazzetta*, 1895, **25**, i, 110—114).—The essential oil of *Cannabis indica*, purified by distillation in a current of steam and extraction with ether, is a mobile liquid boiling at 248—268°; after repeated distillation from metallic sodium in order to remove a stearoptene, it yields a *sesquiterpene*, $C_{15}H_{24}$, as a mobile, colourless oil of aromatic odour, which boils at 256°, and has a density of 0·897 at 15·3°, and is slightly lævorotatory. This soon resinifies on exposure to air, and on adding concentrated sulphuric acid to its chloroform solution the liquid becomes first green, then blue, and red on heating.

The author concludes that the "cannabene," prepared from this essence by Personne, was a mixture. W. J. P.

Constitution of Isonitrosoketones. By Giuseppe Oddo (*Ber.*, 1895, **28**, 1915—1916).—Isonitrosocamphor, whether obtained by the method of Claisen and Manasse, by the action of sodium ethoxide and amylic nitrite on camphor (Abstr., 1889, 619), or by the author's method of treating camphorcarboxylic acid with sodium nitrite (Abstr., 1893, i, 660), behaves in most reactions in the same manner. Both products are converted into camphorquinone by nitrous acid, and into camphorimide by sulphuric acid, and with ethylic iodide the salts yield the same *ethylic* salt, melting at 73°, and crystallising with $\frac{1}{2}$ mol. H_2O; benzoïc chloride also converts them into the same *benzoyl* derivative, melting at 127—128°. Towards acetic chloride, however, the two behave in a totally different manner, the isonitrosocamphor obtained from camphorcarboxylic acid always yielding the *anhydride*, $\left(C_8H_{14}<\begin{matrix}CO\\|\\C:N\end{matrix}\right)_2O$, which melts at 172°, and yields a *monoxime* and a *monohydrazone*; the product obtained by Claisen and Manasse's method, on the other hand, is converted into a substance of unknown constitution melting at 222°, if treated directly with acetic chloride; if, on the other hand, the reaction takes place in ethereal solution it is converted into an isomeride melting at 151°, which dissolves readily in alkalis, and yields liquid *methylic* and *ethylic* derivatives boiling at 270° and 278° respectively. It is no longer converted by nitrous acid into camphorquinone, and has probably the constitution $\begin{matrix}HN\\|\\O\end{matrix}>C<\begin{matrix}C_8H_{14}\\|\\CO\end{matrix}$.

This difference in the behaviour of the isonitrosocamphor obtained by different methods is probably due to the fact that the two compounds are stereoisomerides, the one obtained by the author's method being anti-nitrosocamphor, whilst Claisen's is syn-isonitrosocamphor.

H. G. C.

Campholenic Derivatives. By Auguste Béhal (*Compt. rend.*, 1895, **120**, 1167—1170).—The results described by Tiemann (this vol., i, 426) agree in general with those obtained by the author. The inactive amide prepared by Tiemann by boiling isoamidocam-

phor with acids, has been prepared by the author by the action of hydrochloric acid or hydriodic acid on the active amide. Tiemann's statements, that hydrochloric acid is without action on camphoroxime, and that the production of campholene when campholenic acid is heated with traces of sodium is due to the presence of campholenolactone, do not agree with the author's results (this vol., i, 240 and 241), and it would seem that Tiemann has not distinguished between the two distinct lactones described by the author (this vol., i, 552). The constitution attributed by Tiemann to the active campholenic acids is not in accordance with Guerbet's results (Abstr., 1894, i, 254), nor even with his own observations. C. H. B.

Pyrazolone. A Reply. By FRIEDRICH STOLZ (*J. pr. Chem.*, 1895, [2], **52**, 138—141).—The author replies to v. Rothenburg's recent statements concerning the pyrazolone controversy (this vol., i, 571). A. G. B.

Chlorophyll. Part V. By EDWARD SCHUNCK (*Proc. Roy. Soc.*, 1894, **55**, 351—356; compare Abstr., 1893, i, 41; 1889, 279; 1887, 972).—The author gives the results of the analyses of some of the substances previously described. Phyllocyanin cupric acetate apparently has the composition $C_{67}H_{71}N_5O_7Cu_2$; pure phyllocyanin could not be obtained from this compound.

Analyses of pure phyllotaonin, methyl- and ethyl-phyllotaonin, and phyllotaonin acetate are given. Several formulæ are mentioned which agree with these analyses. J. J. S.

Benzylcysteïne. By F. SUTER (*Zeit. physiol. Chem.*, 1895, **20**, 562—563).—*Benzylcysteïne*, $NH_2{\cdot}CMe(SC_7H_7){\cdot}COOH$, is formed by the interaction of cysteïne hydrochloride, benzylic chloride, and soda at ordinary temperatures. It crystallises in pearly, lustrous plates, and melts and decomposes at 215°. The compound reacts with alkaline copper solution like ethylcysteïne (Abstr., 1892, 1111), and evolves ammonia when boiled with soda. J. B. T.

Pyridine produced during Coffee Roasting. By ADOLFO MONARI and L. SCOCCIANTI (*Gazzetta*, 1895, **25**, i, 115—117).—On heating Mocha coffee at 260°, a distillate is obtained which yields an oil when treated with potassium carbonate solution; the oil consists of pyridine and a small proportion of homologues of this base. Neither ethylamine nor trimethylamine could be detected. W. J. P.

Synthesis of Isoquinoline Derivatives. By PAUL FRITSCH (*Annalen*, 1895, **286**, 1—26; compare Abstr., 1893, i, 366 and 427).—1 : 3-*Hydroxybenzylideneamidoacetal*, $OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}CH_2{\cdot}CH(OEt)_2$, crystallises from light petroleum in snowy needles and melts at 71°. 1 : 3-*Methoxybenzylideneamidoacetal*, boils at 222° under a pressure of 50 mm.; under the same pressure, 1 : 3-*ethoxybenzylideneamidoacetal* boils at 228·5°, and *piperonylideneamidoacetal* at 238·5°.

2-*Hydroxyisoquinoline* is obtained in a quantity approaching 80 per cent. of that required by theory when 1 : 3-hydroxybenzylideneamidoacetal is heated for 5 hours with a mixture of concentrated

sulphuric acid (5 parts) and water (1 part); after remaining for several hours at the ordinary temperature, the liquid is diluted with water and added to a dilute solution of sodium carbonate (compare Pomeranz, Abstr., 1894, i, 552). The base crystallises from alcohol in lustrous leaflets and melts at 226—227°; it dissolves sparingly in organic solvents, but is readily soluble in acids and alkalis, although insoluble in alkali carbonates. The *hydrochloride* crystallises from alcohol in prisms, and melts at 181—190°; the *platinochloride* forms reddish-yellow needles, and melts and decomposes at 252° when rapidly heated.

2-*Methoxyisoquinoline* is prepared from 1 : 3-methoxybenzylideneamidoacetal and sulphuric acid of the concentration already mentioned, the liquid being extracted with ether after treatment with alkali. The base melts at 49°, and boils at 194—195° under a pressure of 50 mm.; it dissolves readily in common solvents, and crystallises from light petroleum in small needles. The *hydrochloride*, which tastes bitter, crystallises from alcohol in prismatic needles, and melts at 221°; the *sulphate* crystallises from alcohol in prisms, and the *dichromate* separates from hot water in small needles. The *platinochloride* melts and decomposes at 235—236°, and crystallises in delicate needles; the *picrate* crystallises in small, lemon-yellow needles, and melts at 194—195°. The *tartrate* is obtained as a powder on treating an acetone solution of the base with tartaric acid dissolved in a mixture of acetone and alcohol; the salt separates from an aqueous or alcoholic solution in a gelatinous condition. The *methiodide* crystallises in deep yellow prisms and melts at 196—197°; the *ethiodide* forms pale yellow prisms and melts at 178—179°.

2-*Ethoxyisoquinoline* melts at 7—9°, and boils at 199° under a pressure of 50 mm., its sp. gr. is 1·0768 at 20°/4°, and its refractive power $[n]_D = 1{\cdot}6062$, or $M = 55{\cdot}5$. The *hydrochloride* crystallises from alcohol in slender needles, and melts at 223°; the *sulphate* forms prisms, and the *dichromate* crystallises from hot water in lustrous, yellowish-brown prisms which darken on exposure to air. The *platinochloride* separates in slender needles, and melts at 245°. The *picrate* crystallises from hot water in slender, yellow needles, and melts at 202°; the *methiodide* and *ethiodide* melt at 193—194° and 122—123° respectively.

2 : 3-*Methylenedioxyisoquinoline*, $CH_2{:}O_2{:}C_9NH_5$, is prepared by dissolving piperonylideneamidoacetal in sulphuric acid (5 parts) mixed with water (1 part), saturating the liquid with hydrogen chloride at 0°, and allowing it to remain in a closed vessel at this temperature for 10 days, and subsequently for four days at the ordinary temperature. The base crystallises from light petroleum, melts at 124°, and boils at 214—216° under a pressure of 50 mm., a portion becoming decomposed. The *hydrochloride* crystallises from alcohol in needles, and melts and decomposes at 250°; the *platinochloride* forms lustrous, gold-coloured needles, and melts at 243°, undergoing decomposition. The *picrate* crystallises in yellow needles, and chars when heated; the *methiodide* separates from alcohol in yellow prisms, and melts at 244°.

The foregoing quinoline derivatives, in dilute acid solution,

exhibit fluorescence, bluish-violet in the case of methoxy- and ethoxy-isoquinoline, whilst solutions of methylenedioxyisoquinoline show green fluorescence; hydroxyisoquinoline exhibits bluish-violet fluorescence only in concentrated sulphuric acid solution.

Tetrahydro-derivatives have been prepared by reducing methoxy-isoquinoline and ethoxyisoquinoline in alcoholic solution with sodium, and also from the methiodide and ethiodide of these compounds by means of tin and hydrochloric acid. The physical properties of the tetrahydro-derivatives, together with the melting-points of their salts, are collected in the following table:—

	B. p. (under 50 mm.).	Sp. gr. at 20°/4°.	$[\alpha]_D$ at 20°.	*M.*	Hydrochloride.	Platinochloride.
					m. p.	m. p.
2-Methoxytetrahydroisoquinoline	184—186°	1·0987	1·5638	49·41	228—229°	202°
2 : 2′-Methoxymethyltetrahydroisoquinoline..	179°	1·0503	1·5481	53·60	201—202°	206°
2 : 2′-Methoxyethyltetrahydroisoquinoline	188—189°	1·0352	1·5415	58·08	219—220°	184—185°
2-Ethoxytetrahydroisoquinoline.....	194—195°	1·0916	1·5523	51·90	256°	218°
2 : 2′-Ethoxymethyltetrahydroisoquinoline	187—188°	1·0255	1·5389	58·40	196—197°	209°
2 : 2′-Ethoxyethyltetrahydroisoquinoline	197—198°	1·0309	1·5417	62·63	210—211°	170—171°

2 : 3-*Methylenedioxy*-2′-*methyltetrahydroisoquinoline* (hydrohydrastinine) is obtained by reducing the methiodide of methylenedioxyisoquinoline in alcoholic solution with tin and hydrochloric acid; after removing the metal in the form of sulphide, the liquid is rendered alkaline and extracted with ether. It separates from light petroleum in tabular crystals and melts at 60—61°. Careful comparison of the base and its derivatives with hydrohydrastinine (Freund) and its salts establishes their identity, and the product of oxidation of methylenedioxymethyltetrahydroisoquinoline is identical in every respect with hydrastinine obtained from hydrastine.

In order to show that condensation of meta-substituted derivatives of benzylideneamidoacetal takes place in the para-position with regard to the substituent, the oxidation of 2 : 2′-ethoxymethyltetrahydroisoquinoline was undertaken. The action of a 3 per cent. solution of potassium permanganate in presence of alkali gives rise to an *acid*, $C_{12}H_{13}NO_5 + H_2O$, which crystallises from chloroform and melts at 100°; the *barium* salt has the composition $(C_{12}H_{12}NO_5 + H_2O)_2Ba$. Chromic acid oxidises this acid to *ethoxymethylphthalimide*, $OEt\cdot C_6H_3<\begin{matrix}CO\\CO\end{matrix}>NMe$, which crystallises from alcohol in prismatic needles, and melts at 110—111°. *Ethoxyphthalic acid* [COOH : COOH : OEt = 1 : 2 : 5] is obtained from the foregoing substance by treating it with a boiling solution of potash (33 per cent.) for 15 minutes; it crystallises from hot water in leaflets, containing

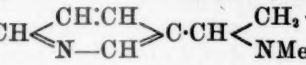
$1H_2O$, and becomes anhydrous at 100°, melting at 163°. If kept for some time at 220°, the substance melts at 80°. M. O. F.

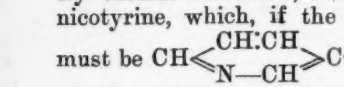
Phenylpyrroline and Pyridylpyrroline; Constitution of Nicotine. By Amé Pictet and Pierre Crépieux (*Ber.*, 1895, **28**, 1904—1912).—1-*Phenylpyrroline*, $\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\!\!>\!NPh$, is obtained by the distillation of normal aniline mucate, the yield being fairly good. It has all the properties described by Köttnitz (this Journal, 1873, 163), boils at 234°, is very volatile in a current of steam, and colours pine-wood violet in presence of alcohol and hydrochloric acid. When distilled through a tube heated to dull redness, it is, to a large extent, converted into an isomeric phenyl derivative, in which the latter group is combined with carbon. It can be separated from unaltered 1-phenylpyrroline by fractional crystallisation from light petroleum, in which the latter is more readily soluble. It forms nacreous plates, which become pink on exposure to air, melts at 129°, boils at 271—272° under 726 mm. pressure, volatilises in a current of steam, and sublimes in broad plates. It colours pine-wood violet, and, on oxidation, yields benzoic acid, proving that the phenyl group is combined with one of the carbon atoms; it is, as yet, uncertain whether it is a 2- or 3-phenyl derivative, although, as Ciamician and Silber (Abstr., 1887, 597) have shown that 1-acetylpyrroline under similar conditions passes into 2-acetylpyrroline, it is probable that in the case of the phenyl derivative the 2-phenylpyrroline is also formed.

1 : 3-*Pyridylpyrroline*, $CH\!<\!\begin{matrix}CH{\cdot}CH\\ |\\ N{=}HC\end{matrix}\!\!>\!C{\cdot}N\!<\!\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}$, is obtained in a similar manner to the phenyl derivative by distilling a mixture of 3-amidopyridine and mucic acid; the product contains large quantities of unaltered amidopyridine, which may be partially removed by treating the product with water; the residual oil is then boiled with acetic anhydride, and the 3-acetamidopyridine thus formed separated from the pyridylpyrroline by fractional distillation. The former crystallises in lustrous plates, melts at 131°, boils at 326—327°, and, like amidopyridine, colours pine-wood orange-yellow. 1-Pyridylpyrroline boils at 250·5—251° under 730 mm. pressure, has a sp. gr. of 1·044 at 24°/4°, and an odour somewhat resembling that of benzaldehyde; it colours pine-wood blue. The *picrate* crystallises in yellow needles, melting at 178°; the *platinochloride* in pale yellow plates, melting and decomposing at 190°; the *mercurochloride* in long, white needles, melting at 189°; and the *methiodide* in small, white needles, melting at 241°. On heating, it undergoes intramolecular change even more readily than the phenyl derivative, yielding a *c*-phenylpyrroline, which is separated from the unaltered base by washing with light petroleum, and then dissolving the residue in benzene and precipitating with light petroleum. It forms a crystalline mass of microscopic, white needles, melting at 72°, gives an orange-red coloration with very dilute ferric chloride, and a dark blue pine-wood reaction. The *picrate* crystallises in well-developed yellow prisms, melts at 182°, and is much less soluble in

boiling water than the picrate of the 1-pyridyl derivative; the *platinochloride*, $(C_9N_2H_8)_2,H_2PtCl_6 + 2H_2O$, forms golden-yellow needles, and decomposes at 150° without melting; the *mercurochloride* crystallises in small, pale yellow needles, melting at 178—179°; and the *methiodide* in similar crystals, melting at 170—171°. The *potassium* derivative, obtained by the action of metallic potassium at the melting point, is a light grey, crystalline powder.

The recent investigations of Pinner and others have shown that nicotine is probably a 1 : 2 : 3-methylpyridylpyrrolidine,



By careful oxidation, nicotine loses 4 atoms of hydrogen forming nicotyrine, which, if the above constitution of nicotine be correct, must be  , or is the 1-methyl derivative of the authors' synthetical pyridylpyrroline, if the pyridyl group really occupies the 2-position. When the potassium salt of the synthetical base is heated with methylic iodide, the potassium is displaced by methyl, but at the same time, it combines with methylic iodide, yielding the *methiodide of* 2 : 3-*pyridylpyrroline;* this crystallises in long, yellow needles, melts at 207°, and colours pine-wood green. A direct comparison of this substance with the methiodide obtained from nicotyrine has shown that in all probability they are identical, but to prove this definitely, it is necessary to obtain larger quantities of the synthetical compound. H. G. C.

Nicotine. By ADOLF PINNER (*Ber.*, 1895, **28**, 1932—1935).—A criticism of the recent paper of Oliveri (this vol., i, 433), in which it is shown that the compounds obtained by the latter by the action of bromine on powdered nicotine hydrobromide have not the constitution assigned to them, but are in reality mixtures. The constitutional formula suggested by Oliveri, which had already been considered by the author, is quite incompatible with the recent results of the chemical and physical investigation of nicotine.

H. G. C.

Action of some Inorganic Cyanides on Chlorocaffeïne. By M. GOMBERG (*Amer. Chem. J.*, 1895, **17**, 403—420).—The product obtained by heating bromocaffeïne with an alcoholic solution of potassium cyanide is identical with that previously obtained by similar treatment of chlorocaffeïne (Abstr., 1893, i, 375), and is shown to be *caffeïnecarboxylamide.* When heated at 250° with phosphoric anhydride, it yields *cyanocaffeïne*, $C_8H_9N_4O_2{\cdot}CN$, which crystallises in small prisms, melts at 151°, and freezes at 109—110°; it sublimes unchanged, and dissolves in hot water, hot alcohol, methylic alcohol, chloroform, and hot benzene, but not in ether. Cyanocaffeïne is only slowly converted into the amide when boiled with water or dilute alcohol, unless a little potassium cyanide is present, when the conversion is rapid and complete.

Chlorocaffeïne was heated with a solution of potassium cyanide in

(1) absolute alcohol; (2) water; (3) methylic alcohol; also with mercuric cyanide in alcohol, and with potassium mercuric cyanide in alcohol; furthermore, chlorocaffeïne was fused with potassium cyanide. It was found, however, that none of these methods yields so large a proportion of cyanocaffeïne as that obtained by dehydrating the carboxylamide with phosphoric anhydride.

By treating cyanocaffeïne with sodium in amylic alcohol, crystals of an organic base, probably caffeylmethylamine, $C_8H_9N_4O_2{\cdot}CH_2{\cdot}NH_2$, were prepared, but were not fully identified.

Caffeïnecarboxylic acid, $C_8H_9N_4O_2{\cdot}COOH$, may be prepared from the amide by dissolving it in sulphuric acid (1 : 1) and passing a stream of nitrous anhydride through the solution until a few drops give no immediate precipitate on the addition of water; water is then added to precipitate the carboxylic acid. It forms silky, acicular crystals of sour taste and bitter after taste, and melts and decomposes at 225—226°; it dissolves in hot water and hot alcohol, but not in chloroform, carbon bisulphide, or benzene. The *sodium* salt, with $2H_2O$; *potassium*, with $2H_2O$; *calcium*, with $5H_2O$; *barium*, with $5H_2O$; *copper*, with $4H_2O$; and the *silver* salt are described. The *methylic* salt melts at 201·5° (uncorr.), and sublimes unchanged; the *ethylic* salt melts at 207—208°, and also sublimes unchanged.

The author concludes by pointing out that the above compounds are the first compounds of caffeïne in which the carbon of the CH-group has been linked to a new carbon atom. The ease with which caffeïnecarboxylic acid loses carbonic anhydride when heated is in accord with the general nature of many acids in which the carboxyl group is attached to an unsaturated carbon atom. Thus the position of the carboxyl group is, to a certain extent, established and E. Fischer's formula for caffeïne confirmed. A. G. B.

New Alkaloïd contained in Coffee. By Pietro Palladino (*Gazzetta*, 1895, **25**, i, 104—110).—The author extracts the bases from ground coffee berries by repeated boiling with milk of lime, filters, treats the liquor with lead acetate, and repeatedly extracts with chloroform to remove the caffeïne. The aqueous liquor is then concentrated with the addition of sulphuric acid, and, after dilution and filtration, is precipitated with Dragendorff's reagent; a well-crystallised double *iodide* of bismuth and caffearine (Abstr., 1894, i, 214) is thus ultimately obtained.

Caffearine hydrochloride, $C_{14}H_{16}N_2O_4,HCl + H_2O$, crystallises in small, colourless needles, loses water at 110°, and melts at 180° with decomposition; it is very soluble in water, as is also the *platinochloride*, $C_{14}H_{16}N_2O_4,H_2PtCl_6$, which crystallises in long, red prisms.

Caffearine, $C_{14}H_{16}N_2O_4$, crystallises in colourless, deliquescent needles, which slowly turn red in dry air, and melt and decompose at 140°; it does not sublime, has a feebly alkaline reaction, but no circular polarisation in solution. Its physiological action has not yet been fully investigated, but it seems to act as a narcotic poison. W. J. P.

Narceïne. By MARTIN FREUND and HUGO MICHAELS (*Annalen*, 1895, **286**, 248—255); compare Abstr., 1894, i, 58 and 477).—*Narceïneamide*, $C_{23}H_{28}N_2O_7 + H_2O$, is the substance specified in D.R.P. 58,394, under the name of methylnarcotamide; it is obtained by allowing narcotine methiodide to remain in contact with alcoholic ammonia for several days. It crystallises from dilute alcohol, and contains $1H_2O$, which is removed at 100°; the substance, when anhydrous, melts at 78°, and in the hydrated condition at 125°, becoming solid above this temperature, and finally melting at 178°. The *hydrochloride* melts at 236—237°.

Narceïneimide, $C_{23}H_{26}N_2O_6$, crystallises from alcohol in small, yellow needles, and melts at 150°; its *hydrochloride* melts at 239—240°; the *nitrate* at 224—225°; the *hydrogen sulphate* at 194—195°; and the *methiodide* at 244—245°.

Narceonimide, $C_{21}H_{19}NO_6$, is obtained by heating the methiodide of narceïneimide with 30 per cent. aqueous potash, trimethylamine being eliminated; it crystallises from glacial acetic acid in slender, yellow needles, and melts at 177·5—178·5°. The *phenylhydrazide anhydride* of narceonic acid, $C_{27}H_{24}N_2O_6$, is formed when the alcoholic solution of the acid is boiled with phenylhydrazine; it crystallises from a mixture of alcohol and glacial acetic acid in white prisms, and melts at 181—182°. The *oxime anhydride*, $C_{21}H_{19}NO_7$, crystallises from glacial acetic acid in needles and leaflets, and melts at 201—202°.

Monobromonarceonic acid, $C_{21}H_{19}BrO_8$, is obtained by adding bromine (1 mol.) to narceonic acid in glacial acetic acid; it separates from alcohol in white crystals, and melts at 171—172°.

Tribromonarceonic acid is formed when excess of the halogen is employed; it melts at 231—232°. M. O. F.

Hydrocinchonine, Hydrochlorocinchonine and Hydrochlorapocinchonine. By OSWALD HESSE (*Ber.*, 1895, **28**, 1424—1426).—The author criticises some of the results published by Konek (this vol., i, 579). It is shown that commercial cinchonine always contains more or less hydrocinchonine, and that this is beyond doubt identical with Zorn's crystalline hydrocinchonine.

When, however, pure cinchonine is reduced with sodium amalgam, an amorphous hydrocinchonine, $C_{19}H_{26}N_2O$, is obtained. According to David Howard the same product can be obtained from cinchonidine, and it must therefore be a tetrahydrocinchonicine. As v. Miller and Rohde (*Annalen*, **276**, 109) have shown that cinchonicine has a very different molecular structure from cinchonine, it follows that this amorphous reduction product cannot be a simple hydrocinchonine.

If cinchonine is heated with concentrated hydrochloric acid during 48 hours at 85°, or for a shorter time at 100°, the chief product is hydrochlorocinchonine. As this compound is not acted on by tin and hydrochloric acid, it follows that it, and not hydrocinchonine, is the chief product obtained on treating cinchonine with these reducing agents. This hydrochloro-base is identical with the hydrochlorocinchonine of Comstock and Königs (Abstr., 1887, 1124); but is not, as Konek states, identical with Zorn's chlorocinchonide and

Hesse's hydrochlorapocinchonine; Zorn's chlorocinchonide is really an additive compound formed by the addition of hydrogen chloride to apocinchonine, and is, therefore, hydrochlorapocinchonine. It is doubtful whether Konek's chlorocinchonide is hydrochlorocinchonine or hydrochlorapocinchonine. The two hydrochloro-bases may be distinguished by means of their behaviour with alcoholic potash; when treated with this reagent, hydrochlorocinchonine gives α-isocinchonine, which is dextro-rotatory, whereas hydrochlorapocinchonine gives β-isocinchonine, which is lævo-rotatory. J. J. S.

Action of Sodium and Amylic Alcohol on Cinchonine. By Fr. Konek Edler von Norwall (*Ber.*, 1895, **28**, 1637—1641; compare this vol., i, 579).—When cinchonine is treated with sodium in boiling amyl alcoholic solution it takes up four atoms of hydrogen; and the product, when treated with potassium nitrite and sulphuric acid, yields *tetrahydrocinchonine nitrite*, $NO\cdot C_{19}H_{25}N_2O,HNO_2$, which crystallises in silky, yellow needles. The free base instantaneously yields a colourless additive compound with methylic iodide, from which fact the deduction is drawn that the four hydrogen atoms attach themselves to the quinoline ring, that nitrogen atom remaining unaffected which, in cinchonine itself, readily takes up methylic iodide, &c., to form colourless derivatives. C. F. B.

Constitution of Aconitine. A Reply.—By Wyndham R. Dunstan and Francis H. Carr (*Ber.*, 1895, **28**, 1379—1382).—A reply to Freund's criticisms (*Ber.*, 1895, **28**, 192) on the authors' work. J. J. S.

Chrysanthemine. By Francesco Marino-Zuco (*Gazzetta*, 1895, **25**, i, 255—262).—On heating chrysanthemine at 150—160° with concentrated hydriodic acid, decomposition suddenly occurs and methylic and ethylic iodides distil over; the residue in the retort contains no chrysanthemine, but on dissolving it in water, decolorising with sulphurous acid, and adding potassium bismuth iodide solution, tetramethylammonium bismuthiodide separates. From the mother-liquor, after precipitating the bismuth and iodine, a *methylpiperidine-carboxylic acid*, $C_5NH_9Me\cdot COOH$, may be separated as its *aurochloride*, $C_7H_{13}O_2N,HAuCl_4$, which crystallises in hard yellow prisms melting at 130°; the acid itself is a syrupy liquid which ultimately solidifies to a hygroscopic crystalline mass. This decomposition of the alkaloïd supports the constitution previously assigned to chrysanthemine by the author (Abstr., 1892, 84) but in view of the optical inactivity of the alkaloïd he considers that the constitution

$$OH\cdot CH_2\cdot \underset{\displaystyle CH_2\cdot C_5NH_9\cdot CO}{\overset{\displaystyle}{CH}}\cdot CH_2\cdot NMe_3 > O,$$

is the more probable. W. J. P.

The Alkaloïds of Cannabis Indica and Cannabis Sativa. By Francesco Marino-Zuco and G. Vignolo (*Gazzetta*, 1895, **25**, i, 262—268).—Various parts of the common hemp (*Cannabis sativa*) and of the Indian hemp (*Cannabis indica*) were exhaustively

extracted by boiling with water acidified with sulphuric acid, and the extract evaporated until it acquired a syrupy consistency, any inorganic salts being removed as they separated. It was then diluted with water, decolorised with animal charcoal, treated with soda, and precipitated with potassium bismuth iodide, the double salt deposited being subsequently converted into the *hydrochloride* of the alkaloïd in the usual way. The salt obtained from both varieties of *Cannabis* forms a colourless, crystalline, deliquescent mass; that from *Cannabis sativa* is physiologically almost inactive, but gives rise in the frog to temporary cardiac depression; the hydrochloride from *Cannabis indica* is, however, highly toxic and causes far greater depression of cardiac activity than the preceding. W. J. P.

Scopoleïne. By W. Lubolдt (*Chem. Centr.*, 1895, i, 61; from *Apoth. Zeit.*, 1894, **9**, 869).—Salicylscopoleïne is best prepared by Liebermann and Limpach's method of heating scopolin with salicylide at 230°, and extracting the base with dilute hydrochloric acid; it crystallises in white needles melting at 105°. The hydrochloride, hydrobromide, sulphate, and aurochloride are described. The *platinochloride* crystallises with $2H_2O$ in orange leaflets melting at 205° and with $1H_2O$ in red needles melting at 212°; numerous analyses show that the base has the composition $C_{15}H_{17}NO_4$. The *acetyl* and *benzoyl* derivatives of scopoleïne are described. W. J. P.

Senecionine and Senecine. By Alexandre Grandval and Henri Lajoux (*Compt. rend.*, 1895, **120**, 1120—1123).—*Senecio vulgaris* contains small quantities of two alkaloïds, which the authors call senecionine and senecine. Both are precipitated by mercuric potassium iodide, and both crystallise readily from chloroform, in which they are easily soluble; senecionine, however, is less soluble in alcohol than senecine, and is only very slightly soluble in ether, which dissolves senecine readily.

Senecionine, $C_{18}H_{26}NO_6$, crystallises in small, rhomboidal tables; it has a feebly bitter taste, and a strongly alkaline reaction, neutralising acids with formation of salts, which do not crystallise readily. Its rotatory power is $[\alpha]_D = -80{\cdot}49°$. With a mixture of ferric chloride and potassium ferricyanide, it yields a precipitate of Prussian blue, and with acidified potassium permanganate, it gives a violet coloration.

Senecine has a very much bitterer taste than senecionine. It crystallises from ether in silky tufts, and forms a hydrogen tartrate, which crystallises readily from water in efflorescent needles. No crystalline hydrogen tartrate of senecionine could be obtained. Senecine yields a precipitate of Prussian blue with a mixture of ferric chloride and potassium ferricyanide, and a violet coloration with acidified potassium permanganate. With sulphuric acid, a yellowish coloration, changing to reddish-brown with a violet tint is obtained; with nitric acid, a violet-red coloration, and a deep violet precipitate; with sulphovanadic acid, a violet-brown coloration.

C. H. B.

Organic Chemistry.

Solubility of Iodoform in Alcohol and Ether. By GUSTAV VULPIUS (*Zeit. anal. Chem.*, 1895, **34**, 465; from *Pharm. Centralhalle*, [2], **14**, 117).—At 17—18°, 1 part of iodoform dissolves in 67 parts of alcohol (of 90·5 vols. per cent.) or in 5·6 parts of ether. At the boiling point, 9 parts of alcohol dissolve 1 part of iodoform. The three forms in which iodoform comes into commerce differ only in the rate at which they dissolve. The statements in the German Pharmacopœia are not quite correct. M. J. S.

Action of Nitric acid on Saturated Hydrocarbons and their Derivatives. By MICHAËL KONOVALOFF (*Ber.*, 1895, **28**, 1852—1865; compare Abstr., 1894, i, 265, 277).—Diisobutyl is converted by dilute nitric acid at 105—110° into a mixture of nitro-compounds, which chiefly consist of *tertiary nitrodiisobutyl*, $NO_2 \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CHMe_2$. This is a yellowish liquid, which boils at 201—202°, has the sp. gr. 0·9396 at 0/0°, and the molecular refraction 44·76. The corresponding *amine* boils at 145°, and forms a *hydrochloride*, which crystallises in tablets or thin needles, melting at 157—160°. When the nitro-compound is further heated with dilute nitric acid at 120—125°, *dinitrodiisobutyl*, $C_8H_{16}(NO_2)_2$, which is also a tertiary compound, is formed; it crystallises in colourless plates, and melts at 124—125°. The *diamine* is a strong fuming base, which absorbs carbonic anhydride from the air and yields crystalline salts.

Dinitrodiisopropyl, which is formed in small quantity in the nitration of diisopropyl, is also a crystalline substance, and melts at 206—208°.

Diisoamyl is also mainly converted into a tertiary nitro-compound by dilute nitric acid. *Nitrodiisoamyl* boils at 125° (pressure = 22·5 mm.), but decomposes when distilled under the atmospheric pressure. It is easily reduced to an *amine*, which boils at 190°.

Nitroisopropylbenzene, which had previously been obtained by the action of dilute nitric acid on isopropylbenzene, boils at 125—127° (pressure = 15 mm.) when pure, and has the sp. gr. 1·1176 at 0/0°. Normal butylbenzene is converted into a *secondary nitrobutylbenzene*, $NO_2 \cdot CHPh \cdot CH_2 \cdot CH_2Me$, by dilute nitric acid; this boils at 151—152° (pressure = 25 mm.), and has the sp. gr. 1·0756 at 0/0°, and the molecular refraction 50·33. When its potassium derivative is treated with bromine, a *monobromide* is formed which melts at 55—56°. The corresponding *amine* boils at 220—220·5°, and yields crystalline salts. *Nitroisobutylbenzene*, $NO_2 \cdot CHPh \cdot CHMe_2$, is obtained in a similar manner to the foregoing compound; it boils at 145—146° (pressure = 25 mm.). The *monobromide* is an oily liquid; the *amine* boils at 213·5—215°, and yields crystalline salts; the *hydrochloride* melts at 275—277°, the *picrate* at 166—168°, and the *oxalate* at 120·5—122°. The *sodium derivative of the nitro-compound* has the

formula $NO_2 \cdot CPhNa \cdot CHMe_2$, and gives characteristic reactions with salts of iron, copper, &c.

Tertiary butylbenzene also yields a nitro-compound, which has not yet been obtained pure.

Nitrodibenzyl, $NO_2 \cdot CHPh \cdot CH_2Ph$, obtained in a similar manner, volatiles slowly with steam. The *hydrochloride* of the *amine* melts at 251·5—252·5°.

Toluene when heated at 100° with nitric acid of sp. gr. 1·12 is converted into phenylnitromethane, a yield of 50 per cent. being obtained. This substance is converted by reduction into benzylamine. Mesitylene is readily nitrated by nitric acid of sp. gr. 1·155 at 100°, and yields *xylylnitromethane*, $C_6H_3Me_2 \cdot CH_2NO_2$, which crystallises in thick, four-sided prisms, melting at 46—47°. It is only slowly dissolved by alkalis. The *amine* boils at 220—221°, and its *hydrochloride* melts at 245—246°.

The facts here recorded confirm the conclusions previously drawn by the author from his experiments on nitration.

The nitro-compounds are best obtained from their metallic derivatives by the action of hydrogen sulphide, boric acid, or carbonic anhydride.

The reduction of the nitro-compounds described above always gives rise to the production of a small quantity of a neutral substance, probably an aldehyde, ketone, or alcohol, in addition to the amine.

A. H.

Reaction for Primary and Secondary Nitro-compounds. By Michaël Konovaloff (*Ber.*, 1895, **28**, 1850—1852).—The reaction with nitrous acid (V. Meyer) is not well shown by nitro-compounds containing more than six carbon atoms; on the other hand, such compounds may readily be detected in the following manner. The substance to be tested is shaken with a little concentrated aqueous potash or sodium ethoxide, and the resulting salt extracted with a little water; the aqueous solution is then placed in a tube along with a small volume of ether or benzene, and ferric chloride added drop by drop, the tube being well shaken after the addition of each drop. A red coloration indicates the presence of a primary or secondary nitro-compound; this coloration is due to the formation of a ferric salt, and it is found that the solubility of the ferric salt in ether, benzene, &c., increases with the molecular weight of the nitro-compound. This reaction is very delicate, and is not given by nitrites.

A. H.

Reactions of Aluminium Amalgam. By Hans Wislicenus and Ludwig Kaufmann (*Ber.*, 1895, **28**, 1983—1986).—The first portion of this paper is a reply to the claims of priority of Radziewanowski (this vol., i, 412) and of Cohen and Ormandy (this vol., ii, 394). In the second portion, it is shown that under certain circumstances aluminium amalgam brings about reduction, even if all traces of water are excluded. Thus nitro-compounds, and all alkylic nitrites and nitrates, are reduced when treated with aluminium amalgam and absolute alcohol from which all traces of water have been removed by previous treatment with aluminium amalgam; the

product contains hydroxylamine derivatives, and also combined aluminium, which separates out as hydroxide on the addition of water.

H. G. C.

Removal of Phosphine from Acetylene prepared from Calcium Carbide. Compound of Silver Acetylide with Silver Nitrate. Preparation of Iodinium Compounds. By CONRAD WILLGERODT (*Ber.*, 1895, **28**, 2107—2115).—Acetylene, prepared by the action of water on calcium carbide, contains phosphine, which can be detected by passing the gas through silver nitrate solution. The white precipitate produced by the acetylene is coloured dark by silver phosphide, whilst phosphoric acid passes into solution. The phosphine may be completely removed by passing the gas through bromine water.

The compound of silver nitrate with silver acetylide can be prepared in a pure state by passing purified acetylene into aqueous silver nitrate; it is a white mass, which can be preserved in the dark for a long time. The temperature of explosion of the compound is about 230°.

When the aromatic iodosochlorides are treated with the compound of silver chloride and silver acetylide, free from silver phosphide, and suspended in water, the chlorides of dialkyliodinium bases are formed. The reactions which occur, for example, when phenylic iodosochloride is used are the following.

(1.) $PhICl_2 + HC{:}CAg,AgCl = CH{:}C{\cdot}IPhCl + 2AgCl.$
(2.) $PhICl_2 + H_2O = PhIO + 2HCl.$
(3.) $CH{:}C{\cdot}IPhCl + 2HCl = C_2H_3Cl_2{\cdot}IPhCl.$

Dichlorethylphenyliodinium chloride, $C_2H_3Cl_2{\cdot}IPhCl$, crystallises in colourless prisms and decomposes at 178—179°. *Dichlorethylparatolyliodinium chloride* crystallises in long needles or prisms, which decompose at 178—179°. Both of these chlorides form platinochlorides.

The nitrates of these bases can be obtained by the action of the chlorides on silver nitrate, or by the action of the iodosochloride on the compound of silver acetylide with silver nitrate. In the latter case, when phenylic iodosochloride is used, *chlorovinylphenyliodinium nitrate*, $C_2H_2Cl{\cdot}IPh{\cdot}NO_3$, is obtained. This substance crystallises in prisms and decomposes at 150—153°

Ethenylphenyliodinium nitrate, $C_2H{:}IPhCl$, is probably formed as a crystalline mass when phenyl iodosochloride acts on the compound of silver acetylide with silver nitrate suspended in chloroform. *Dichlorethylphenyliodinium nitrate* decomposes at 162°.

Dichlorethylphenyliodinium iodide forms needles which melt and decompose at 108°.

A. H.

Acetylene and its Hydrate. By P. VILLARD (*Compt. rend.*, 1895, **120**, 1262—1265).—Acetylene, purified in the same way as nitrous oxide (Abstr., 1894, ii, 379), solidifies when the liquefied gas is allowed to evaporate under atmospheric pressure; the solid melts at −81°,

and the boiling point of the liquid is −83°. Its vapour pressure, in atmospheres, is as follows:—

t	−90°	−85°	−81°	−70°	−60°	−50°	−40°
p	0·69	1·00	1·25	2·22	3·55	5·3	7·7

t	−23·8°	0°	5·8°	11·5°	15·0°	20·2°
p	13·2	26·05	30·3	34·8	37·9	42·8

These values are somewhat higher than those given by Ansdell, but concordant results were obtained with different specimens of the gas and with different fractions of the liquefied gas. It is probable that Ansdell's acetylene contained a small quantity of chlorethylene.

Acetylene crystals have no action on polarised light. The coefficient of solubility of the gas at 0° under a pressure of 4·65 atmos. is 1·6.

Acetylene hydrate forms under the same conditions as the hydrates of nitrous oxide (Abstr., 1894, ii, 278) or carbonic anhydride (this vol., ii, 44); its crystals have no action on polarised light. Its vapour pressure is as follows:—

t	0°	4·6°	7·0°	9·6°	15·0°
p	5·75	9·4	12·0	16·4	33·0

At 16°, the pressure is equal to that of the moist liquefied gas. Acetylene does not combine with ice, and the hydrate is practically stable below −0·5° under ordinary pressure (?). The hydrate has the composition $C_2H_2,6H_2O$, and its heat of formation is +15·4 Cal. (Compare *loc. cit.*) C. H. B.

Combination of Nitriles with Aluminium Chloride. By G. Perrier (*Compt. rend.*, 1895, **120**, 1423—1426).—Hydrocyanic acid, acetonitrile and propionitrile dissolve aluminium chloride with development of heat, yielding crystalline compounds of the general composition $Al_2Cl_6,4X$. If the combination takes place in presence of carbon bisulphide, the products have the composition $Al_2Cl_6,2X$. They are insoluble in carbon bisulphide, carbon tetrachloride and light petroleum, and are rapidly decomposed by moist air and by water with liberation of the nitrile and aluminium chloride.

$Al_2Cl_6,4CH_3{\cdot}CN$ melts at 50—55° and decomposes at about 60°; $Al_2Cl_6,2CH_3{\cdot}CN$ melts at 104—105° and decomposes at about 110°. $Al_2Cl_6,4C_2H_5{\cdot}CN$ crystallises in hexagonal tables which melt at 58—60°, and the liquid decomposes at about 80°; $Al_2Cl_6,2C_2H_5{\cdot}CN$ crystallises in slender needles which melt at 70—80°.

When the acetonitrile and propionitrile compounds are heated, some of the nitrile is given off and at about 360° a limpid liquid distils over and solidifies to crystals of the composition $Al_2Cl_6,CH_3{\cdot}CN$, or $Al_2Cl_6,C_2H_5{\cdot}CN$, as the case may be. The former melts at 145—149°, and the latter at 95°; both are decomposed by water into aluminium chloride and the nitrile.

Benzonitrile, under similar conditions, yields the compounds $Al_2Cl_6,4C_6H_5{\cdot}CN$ melting at 75°, $Al_2Cl_6,2C_6H_5{\cdot}CN$ melting at 85° and

$Al_2Cl_6,C_6H_5{\cdot}CN$ melting at 103—105°. In solubility and general properties, they closely resemble the corresponding compounds in the acetic series.

When dry cyanogen is passed over gently heated aluminium chloride, a brown liquid product is formed with considerable development of heat. It crystallises on cooling and is violently decomposed by water. A similar product seems to be formed in presence of carbon bisulphide.

It seems probable that compounds similar to those described in this paper are formed as intermediate products in Desgrez's process for the preparation of nitriles by the direct combination of cyanogen with hydrocarbons of the benzene series.

Liquid cyanogen chloride seems to form no combination with aluminium chloride, but a supersaturated solution is produced, and when it solidifies the heat developed causes explosive decomposition of the whole mass, with production of solid cyanogen chloride.

C. H. B.

Action of Halogens on Methylic Alcohol. By André Brochet (*Compt. rend.*, 1895, **121**, 130—133).—Chlorine attacks methylic alcohol more readily the higher the proportion of water present. The action of the moist gas on the alcohol of 99·5° in diffused daylight yields mainly formaldehyde. Most probably the primary product is chloromethylic alcohol, $CH_2Cl{\cdot}OH$, which in presence of hydrochloric acid is converted into symmetrical dichloromethylic ether $(CH_2Cl)_2O$. The latter in fact separates as an oily liquid and can be isolated; in presence of water, however, it readily decomposes into hydrogen chloride and formaldehyde. During the action of the chlorine, carbonic anhydride and carbonic oxide mixed with a small quantity of methylic chloride are continuously evolved. The carbon oxides may result from the action of the water on carbonic chloride and the monochloride CHOCl, or from the dehydrating action of the chlorine on the formaldehyde.

If the methylic alcohol is heated, methylal is obtained together with large quantities of methylic chloride, carbonic anhydride, and carbonic oxide, the action being accompanied by flame and by explosions, even in very diffused light.

Bromine in presence of sunlight has practically no action on methylic alcohol at the ordinary temperature; at 100°, the action is slight; at 130—150°, the action is somewhat energetic, the chief product being methylic bromide mixed with some carbonic anhydride, and with small quantities of carbonic oxide and formic acid if the bromine is not in excess.

Iodine at 180—200° attacks the alcohol with difficulty, and small quantities of carbonic anhydride, hydrogen iodide, and methylic iodide are formed. A large proportion of the alcohol is, however, converted into methylic ether, and this compound can readily be prepared by heating the alcohol in sealed tubes with 5 per cent. of iodine.

C. H. B.

Nitro-Alcohols. By Louis Henry (*Compt. rend.*, 1895, **120**, 1265—1268).—Aldehyde and nitromethane dissolve in one another

without any interaction, but in presence of water and a small quantity of potassium carbonate, an action takes place with considerable development of heat and nitroisopropylic alcohol is obtained; in presence of potassium hydroxide the action is violent. Under similar conditions, formaldehyde yields a solid product, and propaldehyde yields secondary nitrobutylic alcohol. Isobutaldehyde reacts somewhat less readily and only in presence of potassium hydroxide. Acetone and nitromethane do not react even in presence of potassium hydroxide.

Nitroisopropylic alcohol is a colourless, limpid, almost odourless liquid, with a very peculiar disagreeable taste. In a mixture of solid carbonic anhydride and ether, it forms a transparent, amorphous mass which after a time becomes crystalline, and melts at about $-20°$; sp. gr. $= 1{\cdot}1910$ at $18°$; boiling point $112°$ under a pressure of 30 mm.; vapour density 3·58. The *acetate*, $OAc{\cdot}CHMe{\cdot}CH_2{\cdot}NO_2$, is a colourless liquid, insoluble in water and boiling at about the same temperature as the alcohol itself; sp. gr. $= 1{\cdot}1670$ at $15°$. The chloride, $CHMeCl{\cdot}CH_2{\cdot}NO_2$, obtained by the action of phosphorus pentachloride, is a colourless liquid which boils at $172°$ under ordinary pressure; sp.gr. $= 1{\cdot}2361$ at $15°$; vapour density 4·23. The nitro-alcohol, like nitromethane, burns with a greenish-yellow flame; with excess of potash, its nitrolic derivative gives the red coloration characteristic of the group $CH_2{\cdot}NO_2$. *Secondary nitrobutylic alcohol* has similar properties.

The product of the reaction between nitromethane and formaldehyde is a crystalline solid which melts at about $140°$, and dissolves in water and most organic solvents, but is only slightly soluble in ether. It may be nitroethylic ether $(NO_2{\cdot}CH_2{\cdot}CH_2)_2O$.

Having regard to the differences of composition between HCHO, $CH_3{\cdot}CHO$, and $COMe_2$, and their different behaviour with respect to nitromethane, it would seem that the tendency of the latter to form additive products is conditioned by the presence of hydrogen in union with carbon in the group CHO. Since all nitroparaffins in which hydrogen is united with the same carbon atom as the NO_2 group are basic like nitromethane, it would follow that all derivatives of this class containing the group, $\cdot CH_2{\cdot}NO_2$, or $:CH{\cdot}NO_2$, should form additive products with aldehydes, but this conclusion has not yet been verified. The same power should also characterise nitro-alcohols which contain either of the groups specified, and as a matter of fact nitrosopropylic alcohol combines readily with formaldehyde or acetaldehyde.

The combining power, with respect to aldehydes, of nitromethane and hydrogen cyanide is as 3 to 1. In nitromethane, as in ammonia, the reaction capacity diminishes in proportion to the displacement of the hydrogen atoms by alkyl radicles.

There is some evidence that in the reaction of nitromethane with aldehydes, more than one product is formed, and not a single product only as in the action between the aldehydes and hydrogen cyanide.

C. H. B.

Allylphosphoric acid. By J. Cavalier (*Compt. rend.*, 1895, **121**, 69—71).—Glacial phosphoric acid dissolves in allylic alcohol with

development of heat, and, after being kept at about 100° for some time, a small quantity of allylphosphoric acid is formed. The best results are obtained by gradually adding phosphoric anhydride to a well-cooled solution of allylic alcohol in its own volume of dry ether. After distilling off part of the ether and adding water, the liquid separates into two layers, the upper of which seems to contain triallylic phosphate, whilst the lower contains allylphosphoric acid, which is isolated by converting it into the barium salt and decomposing the latter with sulphuric acid.

Allylphosphoric acid, $C_3H_5 \cdot H_2PO_4$, is a syrupy, uncrystallisable, dibasic acid, which is neutral to methyl-orange when mixed with one equivalent of alkali, and to phenolphthaleïn when mixed with two equivalents. Many of its metallic salts are described; all the normal allylphosphates which are only slightly soluble in water dissolve readily in dilute acids, and are converted into the hydrogen salts. Most of the salts crystallise readily. C. H. B.

Conversion of d- and l-Linaloöl and of Geraniol into Terpin Hydrate. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1895, **28**, 2137—2140).—If *d*- or *l*-linaloöl is shaken with 20 times its weight of 5 per cent. sulphuric acid for several days at the ordinary temperature, it slowly dissolves, and ether extracts an almost theoretical quantity of inactive terpin hydrate (m. p. 117—118°) from the solution. No intermediate product of hydrolysis was isolated.

Geraniol, also, when treated in a similar manner, yields terpin hydrate, mixed, however, with a small quantity of some syrupy substance. It is thought that these facts point to the constitution, $OH \cdot CMe_2 \cdot [CH_2]_3 \cdot CMe(OH) \cdot CH_2 \cdot CH_2 \cdot OH$, for terpin hydrate. Pinene yields terpin hydrate even more readily when treated with dilute acids, and if Tiemann's formula for pinene is correct, then terpin hydrate would probably be

$$OH \cdot CH_2 \cdot CH_2 \cdot CH(CMe_2 \cdot OH) \cdot CH_2 \cdot CH(OH) \cdot CH_2Me,$$

or $$OH \cdot CH_2 \cdot CH_2 \cdot CH(CMe_2 \cdot OH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot OH.$$

The authors consider that one of the last two formulæ is the more probable, and that terpin, which is inactive, is an intermediate product in the conversion of linaloöl into terpin hydrate. In any case it is thought that terpin hydrate is a saturated open chain compound. J. J. S.

Volemite, a New Heptitol. By EMIL FISCHER (*Ber.*, 1895, **28**, 1973—1974).—Bourquelot described (*Bull. Soc. Mycolog. de France*, v) under the name of *volemite*, a substance which he obtained from the fungus *Lactarius volemus*, and thought to be isomeric with mannitol. He has lately sent a specimen to the author, who finds it to be in reality a heptitol, $C_7H_{16}O_7$. It begins to liquefy at 147°, and melts at 149—151° (corr. 151—153°); its specific rotation $[\alpha]_D = +1{\cdot}92$ at 20°, and it is oxidised by nitric acid, or by bromine and sodium carbonate, to a sugar *volemose*, the yellow *osazone* of which,

$$C_7H_{12}O_5(N_2HPh)_2,$$

melts and decomposes at 196° when heated quickly. The sugar itself was not obtained crystalline. C. F. B.

Ammonia Derivative of d-Glucose. By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 98—105).—*d-Glucosamine*, $C_6H_{13}NO_5$, the molecular weight of which was determined by the cryoscopic method, separates in calculus-like aggregates of small, white needles when a solution of *d*-glucose in methylic alcoholic ammonia is kept for some weeks. The yield is about 50 per cent. of the theoretical. The pure substance, after recrystallisation from methylic alcohol, melts at 127—128°, at the same time decomposing. It is not an aldehyde-ammonia, as stated by Stone (this vol., i, 320), whose analytical results are erroneous, but an isomeride of chitosamine (glucosamine), isoglucosamine, and acrosamine; its basic properties, however, are feebler than those of the last, as it does not form an oxalate. The specific rotatory power in aqueous solution is $[\alpha]_D = +19{\cdot}5°$. *d*-Glucosamine is slowly hydrolysed by water into its proximate constituents, and, when exposed to air, absorbs water and loses ammonia. JN. W.

Discoloration and Coagulation of Milk by Heat. By PAUL CAZENEUVE and HADDON (*Compt. rend.*, 1895, **120**, 1272—1273).—Milk which has been heated at 130° for an hour coagulates, and becomes very acid; it contains formic acid. A solution of lactose (5 : 100) containing a small quantity of sodium carbonate or disodium hydrogen phosphate also becomes yellow, and contains formic acid if heated for an hour at 130°. Formic acid is likewise produced when fresh milk, or the alkaline solution of lactose, is boiled for some time under atmospheric pressure, or when the alkaline lactose solution is heated on a water bath. Caseïn, on the other hand, when heated in sealed tubes at 130° with water containing sodium hydroxide or carbonate, or disodium hydrogen phosphate, undergoes no change.

It follows that the discoloration and coagulation of milk by heat is due to the oxidation of the lactose in presence of the alkaline salts of the milk, one product of the oxidation being formic acid, which precipitates the caseïn, but the latter undergoes no change, except that it is coloured yellow by the products of the decomposition of the lactose. C. H. B.

Origin of Unsaturated Compounds in Plants. By CHARLES F. CROSS, EDWARD J. BEVAN, and CLAUD SMITH (*Ber.*, 1895, **28**, 1940—1945).—When barley straw was distilled with dilute sulphuric acid, furfuraldehyde and volatile acids, chiefly acetic acid, passed over. The water, as it distilled over, was replaced by means of an automatic arrangement; under these circumstances, and with acid of from 10 to 20 per cent. strength, it was found that furfuraldehyde and acetic acid were formed at about the same rate, and are consequently products of the same reaction. No such relation was apparent when the strength of the acid was 30 to 50 per cent. Various celluloses were treated in the same way, and were found to yield volatile acids in addition to varying quantities of furfuraldehyde; in all these cases, however, formic acid formed by far the larger part of the

volatile acids. Since woody matter yields a considerable amount of acetic acid when hydrolysed, whereas cellulose yields but little, it seems that the group CH:CH is present in the former, and this group may have been introduced in the process of lignification, possibly through condensation of an aldehyde group with an acetic acid residue. C. F. B.

Action of Formaldehyde on Amines. By R. Cambier and André Brochet (*Bull. Soc. Chim.*, [3], **13**, 392—418).—When formaldehyde and aqueous ammonia are mixed at −20°, no hexamethylenetetramine is formed, as the product remains liquid; and on removing the excess of water by means of potassium carbonate, a viscous liquid is obtained, which is at once converted into the tetramine by heat, or by the addition of caustic soda. The viscous product probably contains formaldehyde ammonia, $OH{\cdot}CH_2{\cdot}NH_2$, as a small amount of a pyridine base is formed during its conversion into the tetramine.

Hexamethylenetetramine can be sublimed unchanged under very low pressure, and is not affected by water or aqueous ammonia at 150°, but in presence of formaldehyde it is hydrolysed by water at that temperature into methylamine and carbonic anhydride. It dissolves more easily in cold than in hot water, and forms several hydrates. The *hexahydrate*, $C_6H_{12}N_4,6H_2O$, forms very large, transparent, hexagonal prisms, and melts and decomposes at 13·5°. The so-called nitrosopentamethylenetetramine, formed by the action of nitrous acid on hexamethylenetetramine (Delépine, this vol., i, 326), is identical with nitrosotrimethylenetriamine. Hexamethylenetetramine and its salts are decomposed by acids quantitatively into methylamine and carbonic anhydride (compare Delépine, *loc. cit.*); it is a monacid base, perhaps feebly diacid, as it forms both normal and acid salts with the inorganic acids. The *sulphates*, $2C_6H_{12}N_4,H_2SO_4$, and $C_6H_{12}N_4,H_2SO_4$, are both acid to phenolphthaleïn, but the former is neutral to methyl-orange; the latter is readily hydrolysed by water and alcohol into its proximate constituents, the formaldehyde in the latter case combining further with the alcohol to form ethylal. The *normal hydrochloride*, $C_6H_{12}N_4,HCl$, is neutral to methyl-orange and acid to litmus and phenolphthaleïn; but the *acid hydrochloride*, $C_6H_{12}N_4,2HCl$, is acid to all three indicators; as, however, it yields the platinochloride of the normal salt, it is a molecular compound. The normal and acid *nitrates* are similar. All the above salts decompose at their melting points. The *dichromate*, $2C_6H_{12}N_4,H_2Cr_2O_7$, and *tetrachromate*, $2C_6H_{12}N_4,H_2Cr_4O_{13}$, explode when struck or heated.

Formaldehyde condenses with hydroxylamine hydrochloride in cold, aqueous solution to formaldoxime, $CH_2{:}N{\cdot}OH$, or its polymeride, trioximidomethylene, $(CH_2{:}N{\cdot}OH)_3$, with liberation of an equivalent of hydrogen chloride; when the solution is heated, however, the product loses water, and hydrogen cyanide is disengaged.

Formaldehyde condenses with methylamine hydrochloride to form *trimethyltrimethylenetriamine*, $C_6H_{15}N_3$, an oily liquid boiling at 166°, the molecular weight of which was determined by the cryoscopic method. This amine is a tertiary base, whose salts are extremely soluble. It combines readily with alkylic iodides to form crystalline

additive compounds, but it does not form a nitroso-derivative, or condense with formaldehyde. The *hydrochloride*, obtained by passing dry hydrogen chloride into its benzene solution, is extremely deliquescent, and melts and decomposes at 120°. A *platinochloride* was prepared.

Formaldehyde condenses with ammonium chloride in a very complex manner. It is probable that trimethylenetriamine occurs as an intermediate product, together with its condensation products with formaldehyde, and those of the aldehyde with methylamine and dimethylamine, but under certain conditions these products act further with formaldehyde to form carbonic anhydride, methylamine, and trimethylamine. The yields of the amines are quantitative, the former or the latter being produced accordingly as the ammonium chloride or the formaldehyde is in excess. These reactions afford new and extremely convenient methods of preparing the two amines.

Formaldehyde reacts with ammonium carbonate to form hexamethylenetetramine, and with ammonium cyanide to form methyleneamidoacetonitrile.

The authors confirm v. Miller and Plöchl's formula, $(NPh{\cdot}CH_2)_3$, for the condensation product of formaldehyde with aniline. It is highly probable that the trimethylene bases are ring compounds related to the isocyanuric derivatives, and having constitutions such as $NMe<^{CH_2\cdot NMe}_{CH_2\cdot NMe}>CH_2$. The parent substance, trimethylenetriamine, is thus a secondary base, forming nitroso-derivatives, and condensing with formaldehyde. The alkylic derivatives are tertiary bases, and therefore do not form nitroso- or condensation products, but, on the other hand, readily form alkylic iodides.

Triphenyltrimethylenetriamine is readily oxidised by dilute potassium permanganate, or even by air, to phenylic isocyanide, and is broken up by hydrogen cyanide, with formation of phenylamidoacetonitrile, $NHPh{\cdot}CH_2{\cdot}CN$; similarly amidoacetonitrile, or its condensation product with formaldehyde, is obtained from a mixture of formaldehyde and the latter substance. JN. W.

Action of Alkali Sulphites on Fatty Diazo-compounds. By HANS V. PECHMANN (*Ber.*, 1895, **28**, 1847—1850).—Ethylic diazoacetate unites with potassium sulphite to form *potassium ethylic sulphohydrazimethylenecarboxylate*, $COOEt{\cdot}CH<^{NH}_{N{\cdot}SO_3K}$. This substance forms fascicular bundles of prisms, which are very soluble in water, and melt and froth up at 174°; if boiled with water or dilute acid for some time, it is decomposed into hydrazine and ethylic glyoxylate. When the salt is allowed to stand with dilute sulphuric acid at the ordinary temperature, the hydrazine which is formed is accompanied by the products of decomposition of ethylic glyoxalate, namely: formaldehyde, carbonic anhydride, and alcohol. *Dipotassium sulphohydrazimethylenecarboxylate*, $COOK{\cdot}CH<^{NH}_{N{\cdot}SO_3K}$, is formed when the foregoing compound is boiled with aqueous potash.

It crystallises with $1H_2O$ in colourless prisms, and is decomposed by acids with formation of hydrazine. A. H.

Condensation of Aldehydes with Ketones. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, **120**, 1269—1272).—The condensation with acetone, already observed in the case of isovaleraldehyde (Abstr., 1894, i, 224), is a general reaction for the saturated aldehydes of the acetic series, with the exception of formaldehyde and acetaldehyde, which act in a more energetic manner and yield different products.

Propaldehyde and acetone in presence of water and sodium hydroxide react with development of heat, and yield *propylideneacetone*, CHEt:CH·COMe, a liquid which obstinately retains water. Its oxime is a colourless, viscous liquid, which boils at 85° under a pressure of 6 mm.; its acetate boils at 114° under a pressure of 9 mm., and its sp. gr. = 1·0005 at 0°. *Isobutylideneacetone* boils at 153—155°; its oxime is a colourless, oily liquid, which boils at 100° under a pressure of 6 mm., and its sp. gr. = 0·9322 at 0°. The acetate of the oxime is an oily liquid which has a disagreeable odour, and boils at 126° under a pressure of 10 mm.; sp. gr. = 0·9775 at 0°.

The constitution of the non-saturated ketones thus obtained by condensation indicates the possibility of the occurrence of stereoisomerism analogous to that existing between maleïc and fumaric acids, but there is no evidence that the products described are mixtures. They do not react with a mixture of aniline and hydrogen cyanide or of hydrazine and hydrogen cyanide, nor with benzoylhydrazine.

Isoamylideneacetone (*loc. cit.*) condenses with amidoguanidine (compare Baeyer, Abstr., 1894, i, 536), and the nitrate of the *isoamylideneacetoneamidoguanidine* thus has the constitution

$$CHMe_2\cdot CH_2\cdot CH{:}CH\cdot CMe{:}N\cdot C(NH)\cdot NH_2,HNO_3.$$

The corresponding picrate is insoluble in water, but can be crystallised from boiling alcohol.

Œnanthaldehyde and acetone, methyl propyl ketone and propaldehyde, and phenyl methyl ketone and valeraldehyde do not react in a similar manner, from which it would seem that acetone is the only ketone that condenses readily with aldehydes, and that the tendency to condense in the manner described diminishes as the molecular weight of the aldehyde increases, the condensation of the aldehyde itself eventually becoming the dominant reaction. C. H. B.

Condensation of Valeraldehyde. By CHARLES FRIEDEL (*Compt. rend.*, 1895, **120**, 1394).—The author has obtained the α-isopropyl-β-isobutylacraldehyde described by Barbier and Bouveault (following abstract) by the condensation of valeraldehyde in presence of sodium hydroxide. He regards it as identical with the compound of the same composition which has been obtained by several chemists in other ways, but considers that its properties are those of a ketone rather than of an aldehyde. C. H. B.

Condensation of Unsaturated Aldehydes with Acetone. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895,

120, 1420—1423).—Methylethylacraldehyde when mixed with an equal weight of acetone and about 10 times its volume of water containing 0·5 per cent. of sodium hydroxide, and allowed to remain for about 24 hours, yields *methyloctadienone*.

$$CHEt{:}CHMe{\cdot}CH{:}CH{\cdot}COMe,$$

a colourless, mobile liquid, which boils at 97° under a pressure of 8 mm., and has a feeble, aromatic odour; sp. gr. = 0·9170 at 0°. When boiled with its own weight of zinc chloride, it yields pseudocumene.

α-Isopropyl-β-isobutylacraldehyde, $CHMe_2{\cdot}CH_2{\cdot}CH{:}C(CHO){\cdot}CHMe_2$, is obtained by the condensation of i. valeraldehyde under the same conditions as lead to the production of methylethylacraldehyde. It is a colourless liquid, which boils at 73° under a pressure of 6 mm.; its oxime is a colourless, oily liquid, boiling at 115° under a pressure of 8 mm.; sp. gr. = 0·9147 at 0°; the nitrile is a very mobile liquid, boiling at 88—89° under a pressure of 8 mm.; sp. gr. = 0·8637 at 0°.

When mixed with acetone in presence of dilute sodium hydroxide solution, it yields the compound

$$CHMe_2{\cdot}CH_2{\cdot}CH{:}C(CHMe_2){\cdot}CH{:}CH{\cdot}COMe,$$

which, according to the Geneva nomenclature, is 8-methyl-5-isopropyl-3 : 5-nonadiene-2-one. It is a colourless, somewhat viscous liquid, which boils at 123—125° under a pressure of 6 mm. When heated with zinc chloride. it yields metaisopropylcymene, which has an odour resembling that of cymene, and boils at about 220°; sp. gr. = 0·880 at 0°. Some cymene is formed at the same time, most probably as a result of the partial decomposition of the isopropylcymene.

C. H. B.

Action of Hydrogen Peroxide on Acetone and Mesityl oxide. By RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 2265—2269).—Hydrogen peroxide in dilute solution (1 per cent.) has no action on acetone. With a 10 per cent. solution of the peroxide, a small quantity of a crystalline substance is obtained, which melts at 97°, is insoluble in water, acids, and alkalis, but readily soluble in benzene, acetone, and ether; it slowly loses weight when left in the air, and more rapidly over sulphuric acid. The molecular weight, determined in benzene solution, agrees with the formula $(C_3H_6O_2)_3$, thus indicating that the compound is a trimolecular acetone peroxide, with the constitution

$$CMe_2\begin{<}\begin{matrix}O{\cdot}O{\cdot}CMe_2{\cdot}O\\ O{\cdot}O{\cdot}CMe_2{\cdot}O\end{matrix}\end{>}\Big|.$$

An almost theoretical yield of the substance may be obtained by mixing the acetone and hydrogen peroxide (50 per cent.) in molecular proportions, and then adding a drop of phosphoric acid. It is not acted on by acetic anhydride; on warming with dilute sulphuric acid, it is decomposed into acetone and hydrogen peroxide; and is characterised by its explosiveness.

When hydrogen peroxide (10 per cent. solution) is allowed to remain in contact with mesityl oxide for several months at the

ordinary temperature, a crystalline substance, $(C_6H_{11}O_3)_2$, is obtained. It is quite neutral, melts without decomposition at 123°, and is insoluble in dilute acids and alkalis. The constitution is given as $OH\cdot CMe_2\cdot CAc(OH)\cdot CAc(OH)\cdot CMe_2\cdot OH$. J. J. S.

Synthesis of a Methylheptenone Methyl Butylideneethyl Ketone. By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1895, **28**, 2115—2126).—The authors have attempted to synthesise the isoamylideneacetone which they have previously obtained by the oxidation of various members of the geraniol series, especially of geranaldehyde (citral), $CHMe_2\cdot CH_2\cdot CH{:}CH\cdot CMe{:}CH\cdot CHO$ (Abstr., 1894, i, 83).

Various attempts to condense isovaleraldhyde with acetone have shown that the chief product is the diisovaleraldehyde which is obtained by the condensation of two molecules of the valeraldehyde. Small quantities of other compounds were also formed, but they could not be isolated in a pure form; the fraction 160—180° probably contains the isoamylideneacetone,

$$CHMe_2\cdot CH_2\cdot CH{:}CH\cdot COMe,$$

formed by the condensation of 1 mol. of isovaleraldehyde with 1 mol. of acetone.

The authors show that the diisovaleraldehyde prepared by Barbier and Bouveault's method (preceding page) is identical with the diisovaleraldehyde prepared by other methods (compare Friedel, this vol., i, 643, and L. Kohn, *Compt. rend.*, **121**, 259).

When the ethylic isoamylideneacetoacetate of Claisen and Matthews (*Annalen*, **218**, 174) is hydrolysed at a low temperature with a 2·5 per cent. potassium hydroxide solution and the resulting ketonic acid heated, an oil which boils at 255—260° is obtained instead of isoamylideneacetone. This oil is probably a polymeride of the desired ketone; but in any case the reaction indicates that isoamylideneacetone is an extremely unstable substance, and in this respect differs from the natural methylheptenone.

Under special conditions, isovaleraldehyde may be made to condense with acetylacetone to form the diketone,

$$CHMe_2\cdot CH{:}CH\cdot CH(COMe)_2,$$

which distils under atmospheric pressure at 218—220°. It contains a hydrogen atom which can readily be displaced by metals.

The *copper* derivative, $Cu(C_{10}H_{15}O_2)_2$, is readily prepared by shaking an ethereal solution of the ketone with an aqueous solution of copper sulphate to which insufficient alkali for the complete precipitation of the copper has been added; this copper salt is soluble in ether, and is obtained in a crystalline form when the ether is allowed to evaporate.

The *calcium derivative* may be obtained by treating an ethereal solution of the ketone with dry calcium hydroxide, it is more sparingly soluble in ether than the copper compound. *Methyl butylideneethyl ketone*, $CHMe_2\cdot CH{:}CH\cdot CH_2\cdot COMe$, is readily obtained when the copper derivative is mixed with an excess of calcium hydroxide in the form of a cream, and then submitted to steam distillation; it is an oily substance which boils at 163°, and resembles

the natural methylheptenone in most of its physical properties, but the physical constants for the two are by no means identical.

Its *oxime* distils at 122° under a pressure of 28 mm., and at 108—110° under a pressure af 15 mm.

The *semicarbazone* melts at 115° after several recrystallisations, whereas the semicarbazone prepared from the natural product melts at 136—138°. The synthetical methylheptone is also much more readily decomposed by acids and alkalis than the natural product.

As the natural methylheptenone can thus have neither of the following constitutions, $CHMe_2 \cdot CH_2 \cdot CH{:}CH \cdot COMe$ or

$$CHMe_2 \cdot CH{:}CH \cdot CH_2 \cdot COMe,$$

it follows that it must have the formula $CMe_2{:}CH \cdot CH_2 \cdot CH_2 \cdot COMe$ (see following abstract). J. J. S.

Natural Methylheptenone (Methyl Isopropylidenepropyl Ketone), Linaloöl, and Geraniol. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 2126—2137).—From synthetical experiments, it has been shown (see preceding abstract) that the natural methylheptenone, which usually accompanies geranaldehyde, linaloöl, and geraniol in various ethereal oils, and which can readily be obtained by the gentle oxidation of one of these compounds, has the constitution $CMe_2{:}CH \cdot CH_2 \cdot CH_2 \cdot COMe$.

The authors now show that the behaviour of the compound on oxidation supports this formula.

The ketone is oxidised in the cold with a very dilute permanganate solution, according to Wagner's method (Abstr., 1890, 1313). By this means, the double bond is ruptured and two hydroxyl groups are added, thus forming a saturated glycol, which, in its turn, is oxidised by a mixture of chromic and sulphuric acids.

The first product of the oxidation of the natural methylheptenone is a syrup, which, when further oxidised with chromic acid, yields acetone (characterised by its parabromophenylhydrazone, m. p. 94—95°) and levulinic acid (characterised by its phenylhydrazone). This decomposition of the ketone into levulinic acid and acetone agrees with the constitution of the ketone given above.

The two aliphatic alcohols, geraniol, and linaloöl also yield considerable quantities of acetone and of levulinic acid when oxidised in a similar manner. The authors argue that linaloöl must therefore contain the grouping $CMe_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}$, and as it is an optically active alcohol must also contain an asymmetric carbon atom, giving the constitution $CH_3 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe(OH) \cdot CH{:}CH_2$.

Geraniol, on the other hand, is an optically inactive primary alcohol, and hence has the formula $CH_3 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot OH$.

The authors consider that the alcohols, lavendol, nerolol, aurantiol, licareol, &c., are mostly mixtures of geraniol, and dextro- or lævo-linaloöl, with small quantities of other alcohols, which give them their characteristic odours.

Geranaldehyde, which is the aldehyde corresponding with the primary alcohol geraniol, has the constitution

$$CH_3 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CHO.$$

A mixture of several isomeric compounds is obtained when the aldehyde is treated with semicarbazide. The authors have isolated a carbazone which melts at 130—135°, whereas Wallach gives the melting points of the geranaldehyde carbazones as 150° and 160°.

Geranaldehyde is readily converted into cymene by the action of potassium hydrogen sulphate, hydriodic acid, acetic acid, &c., the condensation being preceded by a displacement of the double bonds.

The authors criticise some of the conclusions drawn by Barbier and Bouveault (Abstr., 1894, i, 401) from the oxidation of geranaldehyde and its derivatives in strongly acid solution. They point out that geranaldehyde derivatives are readily converted into terpin derivatives by the action of acids. J. J. S.

α-Diketones. By Ludwig Claisen (*J. pr. Chem.*, 1895, [2], **52**, 76—77).—The author agrees with Fileti and Ponzio's conclusion (this vol., i, 499) that the isonitrosoketones, prepared by Manasse and himself from the ketones $CH_3·CO·CH_2·R$, have the constitution $CH_3·CO·C(NOH)·R$, and not $NOH:CH·CO·CH_2·R$, as he at first suggested. It is curious that amylic nitrite should attack the CH_2 group, for ethylic acetate attacks the CH_3 group, the compound $CH_2Ac·CO·CH_2·R$ being formed. C. F. B.

The Aldol of Diacetyl. By Hans v. Pechmann and Edgar Wedekind (*Ber.*, 1895, **28**, 1845—1847).—The substance previously described as dimethylquinogen, $COMe·CO·CH:CMe·COMe$ (Abstr., 1888, 811), contains 1 mol. of water more than is indicated by the above formula, and is the aldol of diacetyl,

$$COMe·CO·CH_2·CMe(OH)·COMe.$$

It is a thick, odourless, colourless oil, and boils unchanged at 128° under a pressure of 18 mm. It is converted by alkalis into paraxyloquinone, but it has not yet been found possible to convert it into dimethylquinogen. The "trihydrazone" is most probably a substituted pyrazoline of the constitution

$$NHPh·N:CMe·CMe<\begin{matrix}CH_2·C·CMe:N·NHPh\\ \|\\ NPh·N\end{matrix}.$$ A. H.

Constitutional relations of Ricinoleïc and Oleïc acids. By Otto Behrend (*Ber.*, 1895, **28**, 2248—2250).—When the ethylic chloroketostearate of Goldsobel (this vol., i, 81) is treated with sodium amalgam, an *unsaturated acid*, $C_{18}H_{32}O_3$, which melts at 58°, is formed. This is either 9-keto-11 : 12-oleïc acid or 9-keto-12 : 13-oleïc acid. *Chloroketostearic acid* (m. p. 64°) yields the same unsaturated acid when similarly treated. When a boiling acetic acid solution of the chlorketostearic acid is treated with zinc and a little hydrochloric acid, it yields stearolic acid, $C_{18}H_{32}O_2$, thus losing the elements of water besides having hydrogen substituted for the chlorine. Ketostearic acid does not give stearolic acid under similar treatment.

The following formulæ agree with the above reactions.

Ketostearic acid = $CH_3\cdot[CH_2]_7\cdot CO\cdot[CH_2]_8\cdot COOH$.
Stearolic acid = $CH_3\cdot[CH_2]_7\cdot C{:}C\cdot[CH_2]_7\cdot COOH$.
Hydroxyketostearic acid =
$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot COOH$.
Chloroketostearic acid, $CH_3\cdot[CH_2]_5\cdot CHCl\cdot CH_2\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot COOH$.

J. J. S.

Methenic and Methinic acids: Ethereal Cyanacetoacetates. By ALBIN HALLER (*Compt. rend.*, 1895, **120**, 1193—1197).—The author proposes the term *methenic acids* to denote compounds which contain the group $CH_2\bar{R}\bar{R}'$, and *methinic acids* to denote those which contain the group $CH\bar{R}\bar{R}'\bar{R}''$, all the radicles in both cases being electronegative. Compounds containing the group $NH\bar{R}\bar{R}'$ might be called *imidic acids*. This classification into methenic and methinic acids is, however, based on a static view of their constitution, whereas many of the compounds which contain these groups seem to be tautomeric. Brühl and Perkin regard the compounds $CH_2Ac\cdot COOR$ and $CO(CH_2\cdot COOR)_2$ as ethereal ketonic derivatives whilst acetylacetone and the ethereal salts of diacetylacetic and acetylmalonic acids are regarded as unsaturated molecules in which the ketonic function is converted into an enolic function (Abstr., 1894, ii, 433). According to Claisen, the introduction of new negative radicles into the groups CH_2 and CH, increases the tendency to become enolic, whilst the substitution of positive radicles has the opposite effect.

When the ethereal salts of acetocyanacetic acid and its homologues (Abstr., 1888, 818) are brought into contact with phenylhydrazine, they either combine with two molecular proportions of it, or yield acetylphenylhydrazine and its homologues, according to the temperature at which the action takes place. The first reaction can only be explained by assuming that the alkylic cyanacetoacetates have the constitution $R\cdot CH{:}C(OH)\cdot CH(CN)\cdot COOR$, analogous to that attributed by Brühl to ethylic acetylmalonate, their acid functions being due to the presence of the group $\cdot CH(CN)\cdot COOR$ and the enolic group. The compounds with phenylhydrazine will then have the constitution $R\cdot CH{:}C(OH)\cdot C(CN)(COOR)\cdot N_2H_4Ph, N_2H_3Ph$.

The second reaction, which takes place when the substances are heated, is represented by the equation

$$NHPh\cdot NH_2 + R\cdot CH{:}C(OH)\cdot CH(CN)\cdot COOR = NHPh\cdot NH\cdot CO\cdot CH_2R + CH_2(CN)COOR.$$

The compounds with phenylhydrazine are readily obtained by direct combination in presence of ether, and considerable heat is developed by the action. They crystallise readily, but are somewhat unstable, becoming yellow when exposed to light, and are decomposed by ordinary solvents. The compound with *methylic cyanacetoacetate* crystallises in plates which melt at 87°; with *ethylic cyanacetoacetate*, white plates melting at 86°; with *ethylic cyanopropionylacetate*, plates which melt at 87°; with *ethylic cyanobutyrylacetate*, plates which melt at 85°; with *ethylic cyanisobutyrylacetate*, slender

needles melting at 67°. With *ethylic cyanisovaleroacetate* the product melts at 65°, and with the methylic salt at 76·5°.

All these compounds, when heated, yield the corresponding homologue of acetylphenylhydrazine.

Butyrylphenylhydrazine forms flattened needles which melt at 104°, and are soluble in boiling water and ordinary solvents. *Isobutyrylphenylhydrazine* forms white plates melting at 143°. *Isovalerylphenylhydrazine* forms transparent, rhombic tables which melt at 112°.

C. H. B.

Electrical Conductivity of some β-Ketonic Ethereal Salts. By J. GUINCHANT (*Compt. rend.*, 1895, **120**, 1220—1223).—For acetylacetone, by Kohlrausch's method, $k = 0{\cdot}00015$ at 25°. Methylic and ethylic acetoacetates, methylic malonate, and methylic cyanacetate, malononitrile, methylic acetylmalonate, and ethylic diacetoacetate show conductivities which are somewhat feeble, but tend to increase with time, especially in the case of the last two compounds, probably owing to interaction with water. It is especially noteworthy that the only compounds which show any decided conductivity are those which are regarded by Brühl and by Perkin as containing the group C·OH, which is found in the carboxylic acids, phenols, normal cyanic acid, α-hydroxyquinoline, &c. Ethylic acetoacetate and ethylic malonate, which contain the ketonic group, are practically non-conductors.

The sodium salts of the cyanomethenic acids (preceding abstract), on the other hand, show a normal conductivity, and, like acetylacetone, obey Ostwald's law (k = const.) as closely as could be expected, having regard to the fact that the compounds have both an acidic and an ethereal function. In those cases where the heats of neutralisation have been determined, the chemical activity deduced from the thermochemical results agrees with that deduced from the conductivity.

As a rule, in series of homologous acids, the value of k, and consequently the chemical activity, diminishes as the atomic weight increases.

C. H. B.

Preparation and Conductivity of Alkylic Cyanomethinates. By J. GUINCHANT (*Compt. rend.*, 1895, **121**, 71—73; compare preceding abstract).—The compounds described were prepared by Haller's method of acting on an alkylic sodiocyanacetate with an acid chloride. *Methylic cyanopropionylacetate* forms crystals which melt at 39—40°; it boils at 130° under a pressure of 43 mm. *Methylic cyanobutyrylacetate* crystallises in needles melting at 0°, and boils at 135·5° under a pressure of 25 mm.; the *isobutyryl* compound forms octahedral crystals melting at 36—37°, and boils at 139° under a pressure of 48 mm. *Propylic cyanacetoacetate* melts at 35—36° and boils at 133° under a pressure of 25 mm.; the *isobutylic* salt does not crystallise at −15°, and boils at 142° under a pressure of 32 mm.; the *amylic* salt does not crystallise at −15°, and boils at 168° under a pressure of 46 mm. All these compounds give a red coloration with ferric chloride solution, and form insoluble cupric salts; they displace acetic acid from its zinc and silver salts and form

white precipitates insoluble in acetic acid. The sodium salts crystallise as hydrates; the anhydrous salts are more deliquescent the higher their atomic weights.

The conductivity of solutions of these ethereal salts indicates that they are monobasic acids. The difference μ 1024 $-\mu$ 32 varies from 10 to 12; the value of $\mu \propto$ is 351—352, and the value of k varies between 0·50 and 0·73.

The conductivity decreases slowly with time, probably in consequence of the decomposition of the ethereal salt by water. The conductivity of the alkylic cyanomethenates diminishes as the molecular weight increases in the first three terms, but rises in the case of isobutylic cyanacetoacetate. Ostwald observed a similar change at the fourth term in the acids of the acetic series. C. H. B.

Idonic acid, Idose, Iditol, and Idosaccharic acid. By Emil Fischer and Irving Wetherbee Fay (*Ber.*, 1895, **28**, 1975—1983).—These names are used to denote the last remaining members of the group of substances isomeric with mannitol and its derivatives, *l*-idose being itself $OH{\cdot}CH_2{\cdot}\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}{\cdot}CHO$. l-*Idonic acid* is prepared from xylose by means of hydrocyanic acid, in the same way as *l*-gulonic acid (Abstr., 1891, 667), the mixture being allowed to remain 6—10, instead of 2, days. A mixture of *l*-idonic and *l*-gulonic acids is obtained, and these are separated by means of their brucine salts, which are soluble in 200 and 50 parts respectively of methylic alcohol, and melt and decompose at 180—185° (corr. 185—190°) and 155—158°. These two acids can be converted each into the other by heating with pyridine and water at 140°. The salt,

$$(C_6H_{11}O_7)_2Cd,CdBr_2 + H_2O,$$

is characteristic of *l*-idonic acid; the specific rotation is $[\alpha]_D = -3{\cdot}25$ at 20°. By reducing a syrupy mixture of this acid and its lactone, with 2½ per cent. sodium amalgam, l-*idose* is obtained as a syrup which reduces Fehling's solution, but does not undergo fermentation with yeast; its osazone is indistinguishable from gulosazone. By further reduction, it yields l-*iditol*, which was obtained as a syrup; a derivative of this, *tribenzylideneiditol*, $C_6H_8O_6(CHPh)_3$, softens at 215°, and melts at 219—223° (corr. 224—228°), and dissolves in 105 parts of acetone; tribenzylidenemannitol melts at 213—217° (corr. 218—222°), and dissolves in 34·5 parts of acetone. l-*Idosaccharic acid* is obtained by the oxidation of *l*-idonic acid with nitric acid at 50°; it is a syrup, and forms a *copper salt*, $C_6H_8O_8Cu + 2H_2O$; the specific rotation is greater than −100°. This acid replaces the once accepted isosaccharic acid in the group of compounds alluded to above.

Optical antipodes of all the above substances can be prepared, starting from d-*idonic acid*, which is obtained by heating *d*-gulonic acid (itself prepared from saccharolactone) with pyridine and water at 140°. These *d*-compounds resemble the *l*-modifications entirely,

yielding salts with identical composition and melting points, and having a rotation of the same amount but of opposite sign (+).

C. F. B.

Condensation of Aromatic Aldehydes with Cyanacetamide, Malonamide, and Malononitrile. By R. Heuck (*Ber.*, 1895, **28**, 2251—2256; compare Oglialoro, Abstr., 1879, 640; V. Meyer, *Ber.*, **21**, 355; Carrick, Abstr., 1892, 1086; Fiquet, Abstr., 1892, 1340; and Bechert, Abstr., 1894, i, 488).—The author shows that cyanacetamide yields condensation products with benzaldehyde and with furfuraldehyde according to the scheme $R{\cdot}CHO + CH_2(CN){\cdot}CONH_2 = R{\cdot}CH{:}C(CN){\cdot}CONH_2 + H_2O$; and that malonamide and malononitrile react in a similar manner.

α-Cyan-β-furfurylacrylamide, $C_4OH_3{\cdot}CH{:}C(CN){\cdot}CONH_2$, is readily obtained when a mixture of furfuraldehyde is heated with cyanacetamide in molecular proportion, first alone, and then with a small quantity of sodium ethoxide. It crystallises in yellow, glistening needles, melts at 156°, and is only sparingly soluble in cold water, benzene, or chloroform. When treated with phosphorus pentachloride, it yields *furfurylidenemalononitrile*, $C_4OH_3{\cdot}CH{:}C(CN)_2$, which may also be obtained by the action of furfuraldehyde on malononitrile. It melts at 76° and gives a blue coloration with alcoholic potash. The *chloride* of cyanofurfurylacrylic acid, obtained by the action of phosphorus pentachloride on the acid, melts at 79°, and is readily soluble in ether, chloroform, benzene and hot light petroleum. When warmed with water, it is rapidly converted into the acid, with alcohol, it gives the ethylic salt, and with dry ammonia, the amide (see above). The amide, when boiled with a mixture of sulphuric acid (1 part) and water (3 parts), yields the acid; whereas, when boiled with aqueous potash, it gives a substance which is isomeric with the amide; this melts at 150°, is readily soluble in alkalis, and is reconverted into the amide when heated at 160°.

Furfurylidenemalonamide, $C_4OH_3{\cdot}CH{:}C(CONH_2)_2$, which melts at 200°, is only sparingly soluble in alcohol or in water, but readily in acetic acid.

α-Cyanocinnamamide, $C_6H_5{\cdot}CH{:}C(CN){\cdot}CONH_2$, melts at 123°, and is readily soluble in chloroform and alcohol. When treated with phosphorus pentachloride, it yields *benzylidenemalononitrile*,

$$C_6H_5{\cdot}CH{:}C(CN)_2,$$

which may also be obtained by heating benzaldehyde and malononitrile with a small quantity of sodium ethoxide. It crystallises in glistening needles which melt at 87°.

Benzylidenemalonamide, $C_6H_5{\cdot}CH{:}C(CONH_2)_2$, melts at 189—190°, and, when treated with phosphorus pentachloride, yields the corresponding nitrile.

J. J. S.

Nitrofurfuryl Derivatives. By R. Heuck (*Ber.*, 1895, **28**, 2256—2258; compare Priebs, Abstr., 1885, 971).—*Ethylic nitrofurfuryl cyanacrylate*, $NO_2{\cdot}C_4OH_2{\cdot}CH{:}C(CN){\cdot}COOEt$, obtained by adding ethylic furfurylcyanacrylate to well cooled concentrated nitric acid, crystallises in yellow plates, melts at 153°, and is readily soluble in alcohol, benzene, chloroform, and acetic acid.

Nitrofurfurylcyanacrylic acid forms yellow crystals and decomposes at 250°. It is readily decomposed by aqueous or alcoholic alkali, but yields an ammonium salt when ammonia is passed into a cooled solution of the acid in absolute alcohol. The *silver salt* forms a yellow precipitate.

Nitrofurfurylidenemalononitrile, $NO_2 \cdot C_4OH_2 \cdot CH{:}C(CN)_2$, crystallises in yellow, glistening, rhombic plates, and melts at 179°.

Ethylic nitrofurfurylidenemalonate melts at 108°. The author has not succeeded in reducing these compounds to the corresponding amido-derivatives. J. J. S.

Hexachlorobenzene Paradichloride. By Étienne Barral (*Bull. Soc. Chim.*, 1895, [3], **13**, 418—423).—By the action of phosphorus pentachloride on α-hexachlorophenol or tetrachloroquinone, an octochloro-derivative of benzene is formed, whose constitution has an important bearing on that of quinone (compare this vol., i, 655).

The hexachlorophenol (300 grams) is heated with phosphorus pentachloride (215 grams) for 48 hours at 130—135°, or the tetrachloroquinone (32 grams) with the chloride (52 grams) for three days at the same temperature, or, in presence of phosphorus trichloride, for half that time. The product, which solidifies on cooling, is washed with alkali and water and crystallised from benzene, the mixture of needles of hexachlorobenzene and prisms of the dichloride thus obtained being separated by hand.

Hexachlorobenzene paradichloride, C_6Cl_8, forms large, colourless, triclinic prisms or plates, sp. gr. = 2·0618 at 18°, and melts, and to some extent sublimes, at 159—160°. It is insoluble in water, but dissolves in the usual organic solvents. By the action of heat (204°) on the pure substance, or that of chlorine on its carbon tetrachloride solution in presence of antimonic chloride, it is resolved into hexachlorobenzene and chlorine. It is not affected by chlorine in presence of sunlight or of iodine, but is reduced by sodium amalgam to hexachlorobenzene and hydrogen chloride, and is decomposed in a similar manner by prolonged boiling with alcoholic potash, although it is stable towards aqueous potash. Hexachlorobenzene paradichloride is oxidised, completely by nitric acid, and partially by sulphuric acid, to tetrachloroquinone.

The ease with which this octochlorobenzene is formed from, and converted into tetrachloroquinone, leaves no doubt that its constitution is $CCl_2{<}\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}{>}CCl_2$.

Pentachlorophenylic dihydrogen phosphate, $CCl_5O \cdot PO(OH)_2, H_2O$, occurs as a bye-product in both methods of preparation. It forms colourless, transparent crystals, and melts at 224°. Jn. W.

Compounds of Symmetrical Trinitrobenzene. By Pieter van Romburgh (*Rec. Trav. Chim.*, 1895, **14**, 65—70).—Trinitrobenzene is readily separated from its unsymmetrical isomeride by means of its additive compound with dimethylaniline; the base is added to the alcoholic solution of the mixture, and the insoluble additive compound decomposed with dilute hydrochloric acid.

Symmetrical trinitrobenzene forms additive compounds with various nitrogen bases when mixed with them in alcoholic solution. The *brucine* compound, $C_6H_3(NO_2)_3,C_{23}H_{26}N_2O_4$, forms slender, brownish-red needles, having a brilliant lustre, and melts and decomposes at 158°, but no compounds could be obtained with strychnine, morphine, quinine, quinidine, or hydrastine, although colour changes were observed on mixing solutions of trinitrobenzene with daturine, carpaine, and codeïne. The *indole* compound, $C_6H_3(NO_2)_3,C_8H_7N$, forms golden-yellow needles, and melts at 187°; it is stable towards hydrochloric acid, but is partially decomposed into its proximate constituents by benzidine. The *scatole* compound appears to be of the same type; it forms slender, red needles, and melts at 183°. The *pyrroline* compound, $C_6H_3(NO_2)_3,C_4NH_5$, forms long, very brilliant, yellow needles, and melts at 95°, at the same time decomposing into its proximate constituents; it is very unstable, and readily loses pyrroline when dissolved in alcohol, or exposed to the air.

No compounds could be formed with pyridine or quinoline, but a dark red, resinous product is formed when piperidine is heated with trinitrobenzene in alcoholic solution; the piperidine possibly acts as a reducing agent, as a similar action seems to take place with phenylhydrazine.

The *nitrodimethylmetaphenylenediamine* compound,

$$C_6H_3(NO_2)_3,NH_2\cdot C_6H_3(NO_2)\cdot NMe_2\ [NH_2 : NO_2 : NMe_2 = 1 : 2 : 5],$$

forms slender brick-red or crimson needles, and melts at 130°, after softening at 125°. The *nitrotrimethylmetaphenylenediamine* compound forms small red needles, and melts at 144°. JN. W.

Action of Sodium and Caustic Alkalis on Polynitro-derivatives. By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 89—94).—The peculiar colour changes brought about by the action of alkalis on di- and tri-nitrobenzoic acids can hardly be due, as V. Meyer supposes, to the formation of metallic substitution products, for sodium has no action on trinitrobenzene, although this substance also yields a coloration when digested with alkali. The nucleal hydrogen of the di- and tri-nitrobenzenes and their homologues is, in fact, not displaceable by sodium, even when the hydrogen is in the most favourable position, between two meta-nitro-groups; any of the dinitrobenzenes, or symmetrical trinitrobenzene, or its toluene or xylene homologues, may be boiled with sodium in benzene or toluene solution for hours without undergoing any appreciable change.

The *colouring matter* formed by the action of alkalis on trinitrobenzene may be obtained in red crystals, having a green, metallic lustre, by adding cold, concentrated, aqueous potash to a methylic alcohol solution of the nitro-compound. It is probably an additive compound, but is still under investigation. It is slowly decomposed by water into tetranitroazoxybenzene and potassium nitrite. The action of potash on trinitrobenzene is thus remarkably different from that of soda, by which the nitro-compound is decomposed into sodium nitrite and dinitroanisoïl. JN. W.

Influence of the Methyl group on the Properties of Nitro-groups. By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 95—97).—The action of caustic soda on symmetrical trinitrotoluene and trinitro-xylene is much more complex than that on trinitrobenzene, as instead of dinitroanisoïls, brown, amorphous products are formed, soluble in water, and reprecipitated by acids and metallic salts. They are probably azoxy-compounds, formed by reduction of the nitro-compounds.

A similar product is formed by the action of alcoholic potassium cyanide on metadinitrobenzene, and is perhaps due to a similar cause, the entrance of the cyanogen radicle into the 1 : 2 : 3-ethoxycyanonitrobenzene which is formed, resulting from the oxidation of the metal of the cyanide and the hydrogen of the nucleus by other molecules of the dinitro-compound. In the case of dinitrotoluene, the amorphous reduction product is alone formed.

The introduction of a methyl group or groups into the nitrated ring has thus the effect in both cases of favouring the more complex reaction. JN. W.

5-Chlorodihydrometaxylene. By A. KLAGES and EMIL KNOEVENAGEL (*Ber.*, 1895, **28**, 2044—2048; compare this vol., i, 86).—The action of cold dilute nitric acid converts chlorodihydrometaxylene into dimethyl-Δ_2-ketotetrahydrobenzene; if, however, 30 per cent. nitric acid is employed and heated with the substance for 24 hours in a reflux apparatus, nitrochlorometaxylene and symmetrical chlorotoluic acid are formed, a polynitro-derivative and chloropicrin being produced at the same time.

Nitrochlorometaxylene [$Me_2 : NO_2 : Cl = 1 : 3 : 4 : 5$, or $1 : 3 : 2 : 5$], forms colourless crystals, and melts at 48—49°; it dissolves readily in organic solvents, is volatile in an atmosphere of steam, and distils without decomposing.

Symmetrical chlorotoluic acid crystallises from dilute alcohol, and melts at 178°; oxidation of the feebly alkaline solution with potassium permanganate converts it into symmetrical chlorisophthalic acid and hydroxyisophthalic acid.

When chlorodihydrometaxylene is slowly dissolved in ice-cold fuming nitric acid, and then allowed to remain at the ordinary temperature, a vigorous action takes place; equal parts of fuming nitric acid and 15 per cent. fuming sulphuric acid are then added to the liquid, which is boiled in a reflux apparatus for half an hour. On cooling the acid liquid, *symmetrical trinitrochlorometaxylene* separates in lustrous, white leaflets; it crystallises from alcohol in white needles, and melts at 218°. When heated with alcoholic ammonia at 130°, it yields *symmetrical trinitrometaxylidine*, which melts at 206°; this base sublimes when carefully heated, and crystallises from dilute alcohol in yellowish-brown needles. *Symmetrical trinitrophenylamidometaxylene* is obtained by heating trinitrochlorometaxylene with aniline at 150°; it crystallises from alcohol in long, lustrous, yellow needles, and melts at 175°.

Chlorodihydrometaxylene is readily attacked by a cold solution of potassium permanganate, a small quantity of symmetrical chloro-

xylene being formed. This result is also effected by potassium dichromate or a solution of chromic anhydride in glacial acetic acid.

M. O. F.

Trimethylethylbenzene. By PAUL JANNASCH and J. H. WIGNER (*Ber.*, 1895, **28**, 2027—2028).—2 : 4 : 6-Trimethylethylbenzene, $C_6H_2Me_3Et$, is best prepared by heating a mixture of 25 grams of bromomesitylene, 32 grams of ethylic iodide, 14 grams of sodium in thin shavings, and 25 c.c. of xylene at 180° in a paraffin bath. The reaction also takes place in ethereal solution at the ordinary temperature, but the yield is then very small. Ethyltrimethylbenzene is a faint aromatic-smelling liquid boiling at 212—214°; it yields crystalline bromo- nitro- and sulpho-derivatives, which are being further examined.

H. G. C.

Constitution of α-Hexachlorophenol and of Quinone. By ÉTIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], **13**, 423—427).—α-Hexachlorophenol may be regarded either as a substituted ketone of the constitution $CO<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>CCl_2$ or as a pentachlorophenol hypochlorite of the constitution $C_6Cl_5{\cdot}OCl$; but the former view is most in accord with facts. Hexachlorophenol is converted by phosphorus pentachloride into an octochlorobenzene (this vol., i, 652) and not into a hexachlorobenzene. A second hexachlorophenol is known, melting at 46°, which can only be accounted for as a position isomeride, $CCl<\begin{matrix}CCl{\cdot}CCl\\CO{\cdot}CCl_2\end{matrix}>CCl$. Moreover, a hypochlorite would not be stable towards potash, and would not yield tetrachloroquinone on oxidation, as does α-hexachlorophenol. It is true that the hexachlorophenol does not form a bisulphite compound, but this may be explained by the lack of a common solvent for the chlorophenol and the sulphite. Similarly, the absence of a phenylhydrazone may be explained by the fact that the chlorophenol does not contain hydrogen, and acts rather as a chlorinating agent towards the hydrazine. The conversion of α-hexachlorophenol into perchlorodioxydiphenylene and pentachloro phenol is explained equally well by either formula.

Since α-hexachlorophenol has the constitution $CO<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>CCl_2$ and its dichloro-derivative the constitution $CCl_2<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>CCl_2$, the constitution of quinone can only be represented by Fittig's ketonic formula, $CO<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CO$. The only serious argument against this formula, and in favour of Graebe's para-bond formula, was the formation of hexachlorobenzene instead of an octochlorobenzene by the action of phosphorus pentachloride on quinone, and this has now been shown to be due to the decomposition of the octochloro-compound owing to the use of an unnecessarily high temperature.

JN. W.

Action of Zinc Chloride on Resorcinol. By EDOUARD GRIMAUX (*Compt. rend.*, 1895, **121**, 88—100).—When resorcinol is heated for five or six hours at 135—145° with its own weight of zinc chloride,

about half of it is converted into resinous products mixed with small quantities of umbelliferone (hydroxycoumarin) melting at 255°, and another compound melting at 261°. The umbelliferone can be isolated by extracting the product with successive small quantities of boiling water, and the other product is obtained by treating the insoluble residue with boiling toluene.

The compound which melts at 261° forms small colourless needles, insoluble in water but soluble in most organic solvents. It is only slightly soluble in ammonia, but dissolves in potassium hydroxide solution, yielding a non-fluorescent liquid in both cases; it gives no coloration with ferric chloride; is decomposed when heated with zinc chloride or sulphuric acid, and the products show a green fluorescence when dissolved in solutions of alkalis; it yields no fluoresceïn with phthalic anhydride. It has the composition $C_{24}H_{18}O_5$, and seems to be formed from 4 mols. of resorcinol with elimination of $3H_2O$, but it is probable that part of the hydrogen eliminated is derived from the benzene nucleus.

The resinous product insoluble in water and toluene dissolves in alkalis, and yields brown-red solutions with an intense green fluorescence. It seems to be identical with the product obtained by Barth and Weidel by the action of hydrochloric acid on resorcinol at 180°, and erroneously described by them as resorcin ether. C. H. B.

Derivatives of Eugenol. By CARL HELL (*Ber.*, 1895, **28**, 2082—2087).—Dibromeugenol has the same phenolic character as eugenol itself, and readily yields derivatives, whilst dibromeugenol dibromide cannot be converted into salts, ethers, &c.

Dibromeugenol methyl ether, which was first described by Boyen (*Ber.*, **21**, 1393), crystallises in white plates melting at 29·5°. It readily combines with bromine, forming *dibromeugenol methyl ether dibromide*, which crystallises in white, silvery plates melting at 65°. *Bromeugenol methyl ether dibromide*, $C_6H_2Br(OMe)_2{\cdot}C_3H_5Br_2$, is formed by the action of bromine on eugenol methyl ether, although a monobromo-compound cannot be prepared from eugenol itself. It crystallises in lustrous, white needles melting at 77°. It is converted by zinc dust into *bromeugenol methyl ether*, which is a colourless oil boiling at 185° at 40 mm. pressure. It was found impossible to prepare a dibromo-derivative directly from eugenol methyl ether. *Tribromeugenol dibromide* is formed when the dibromo-compound is heated with bromine at 100°, but has not been obtained in the pure state. The *acetate* crystallises in short needles or plates and melts at 137°. *Tribromeugenol acetate* is also a crystalline substance. *Dibromeugenol ethyl ether* is a light yellow oil, which solidifies in the cold to crystals melting at 20°.

The *acetate*, prepared from dibromomethyl eugenol ether dibromide, is converted by oxidation with chromic acid into *dibromoveratric aldehyde*. The brominated ethers of eugenol are converted by alkaline permanganate into brominated veratric acids, which have been made the subject of investigation. *Dibromodimethylprotocatechuic acid* crystallises in plates and melts at 181°; *dibromomethylethylprotocatechuic acid*

melts at 171—172°. These acids will be more fully described in a future publication. A. H.

Derivatives of Isoeugenol. By CARL HELL and B. PORTMANN (*Ber.*, 1895, **28**, 2088—2093).—Isoeugenol is converted by bromine into *bromisoeugenol dibromide*, $OMe{\cdot}C_6H_2Br(OH){\cdot}C_3H_5Br_2$, which melts at 138—139°. If only 1 mol. of bromine be added very carefully to an ethereal solution of isoeugenol, it is possible to obtain *isoeugenol dibromide*, which melts at about 86—87° but is exceedingly unstable. Isoeugenol therefore, in its behaviour towards bromine, differs completely from eugenol, which is at once converted into dibromeugenol dibromide. Isoeugenol methyl ether also readily combines with bromine to form the dibromide, which has been described by Ciamician and Silber (Abstr., 1890, 966). The *dibromide* of the *ethyl ether* melts at 101—104°. The dibromides of the derivatives of isoeugenol are not attacked in alcoholic solution by zinc dust, whilst those of eugenol and its derivatives readily lose their bromine when treated in this way. The dibromide of isoeugenol ethyl ether readily reacts with sodium ethoxide to form a yellowish oil which boils at 177·5° (pressure = 16 mm.), and has the sp. gr. 1·039 at 20°. This substance has the formula $OMe{\cdot}C_6H_3(OEt){\cdot}CH{:}CMe{\cdot}OEt$, and when exposed to the air or treated with dilute acids is converted into a compound of the formula $OMe{\cdot}C_6H_3(OEt){\cdot}CH{:}CMe{\cdot}OH$, which crystallises in large tablets and melts at 56—57°. Methylisoeugenol dibromide, when treated in the same manner, yields an oil which boils at 192—193° (pressure = 15 mm.), and is converted by dilute acids into large crystals melting at 58—59°. This solid compound has the composition $C_6H_3(OMe)_2{\cdot}CH{:}CMe{\cdot}OH$.

Similar results have been obtained with the dibromides of anethoïl and monobromanethoïl, and will be subsequently described.

A. H.

Preparation of the three Nitranilines. By E. BRUNS (*Ber.*, 1895, **28**, 1954—1955).—Aniline is dissolved in 6—8 times its weight of concentrated sulphuric acid, and the solution is kept cooled and stirred in an iron or nickel crucible while it is nitrated with the calculated quantity of nitric acid mixed with an equal volume of sulphuric acid; the temperature should not rise above 0°. The mixture is then poured on to ice and diluted with ice-cold water so long as 2-nitraniline is precipitated; this is purified by one crystallisation from alcohol. The filtrate is neutralised with powdered sodium carbonate; if any resin separates at first, it is filtered off; yellowish-brown 4-nitraniline is first precipitated, and then the 3-compound, which is pure yellow in colour. The colour change is so distinct that there is no difficulty in precipitating first the one compound, and then the other, after filtering off the first; the precipitates are purified by one recrystallisation. In this way, aniline yields 10—15 per cent. of its weight of 2-nitraniline, and from 45—50 per cent. of each of the two isomerides. C. F. B.

Aldoxime Salts. By HEINRICH GOLDSCHMIDT and LUDWIG RÖDER (*Ber.*, 1895, **28**, 2013—2020).—The authors have examined the

lowering of the freezing point of solutions of the sodium salts of the following stereoisomeric aldoximes: syn- and anti-benzaldoxime, syn- and anti-paranisaldoxime, and syn- and anti-metanitrobenzaldoxime, and, from the results obtained, it appears that, in aqueous solutions, the anti-salts undergo almost entirely electrolytic dissociation, whilst the syn-salts, in addition to the electrolytical dissociation, also show a considerable amount of hydrolytic dissociation.

A further series of observations was made as to the alteration of the freezing point caused by the salts in strongly alkaline solutions, the syn-salts employed being those of benzaldoxime, paranisaldoxime, metanitrobenzaldoxime, and propaldoxime, and the anti-salts those of para- and orthanisaldoxime, cuminaldoxime, and metanitrobenzaldoxime. The anti-derivatives all behave in the same manner, the first addition causing a depression of the freezing point, but on further addition of the salt the freezing point rises and finally usually becomes higher than that of the original solution. Of the syn-aldoximes, the metanitrobenzaldoxime behaves in a similar manner, but the others lower the freezing point in proportion to the amount of salt added. This behaviour of the syn-salts must be due to their hydrolytic dissociation, again showing that the syn-aldoximes are much weaker acids than the anti-aldoximes. H. G. C.

Derivatives of the Benzenediazocarboxylic acids. By Arthur Hantzsch and O. W. Schultze (*Ber.*, 1895, **28**, 2073—2082).—The derivatives of the benzenediazocarboxylic acids are obtained from the diazocyanides. The two stereoisomeric diazocyanides yield identical products, which appear to belong to the anti-series.

Paranitrobenzenediazocarbamide, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot CO \cdot NH_2$, is formed when nitrobenzenediazocyanide is boiled with water, and crystallises in long, ruby-red needles which melt at 183°; it may be recrystallised from hot water, but is only sparingly soluble in cold water. *Parachlorobenzenediazocarbamide* is moderately soluble in cold water and crystallises in long, orange-coloured needles melting at 182°. These amides can also be prepared by dissolving the diazocyanides in concentrated sulphuric acid, and by boiling the compounds of the diazocyanides with hydrocyanic acid, as well as the diazobenzenecarboxylic imido-ethers, with water. They are converted by alcoholic potash into the salts of the corresponding acids.

Potassium parachlorobenzenediazocarboxylate, $C_6H_4Cl \cdot N_2 \cdot COOK$, forms lustrous, golden-yellow plates. It may be preserved in the dry state, but decomposes when moist and when its aqueous solution is heated. The salt deflagrates when heated or when placed in sulphuric acid. The free acid is obtained as a yellow precipitate when a solution of the salt is acidified with a mineral acid; it decomposes very rapidly, chlorobenzene being among the products formed. *Potassium paranitrobenzenediazocarboxylate* crystallises in brown needles. The free acid is slightly more stable than the chlorinated acid, but could not be analysed.

The diazocyanides dissolve in alcohol with formation of the corresponding imido-ether of a benzenediazocarboxylic acid. The *ethylimido-ether of nitrobenzenediazocarboxylic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C(NH){\cdot}OEt,$$

crystallises in orange-red needles melting at 73°. The corresponding *methylimido-ether* melts at 128—129°. These compounds do not produce any colouring matter with β-naphthol or R-salt. The *methylimido-ether of chlorobenzenediazocarboxylic acid* forms yellowish-brown needles melting at 69°. Anti-nitrodiazobenzene cyanide reacts in a remarkable manner with β-naphthol, a yellowish-brown reduction product of the cyanide, which has the formula $C_7H_5N_4O_2$, being formed along with a compound of the formula $C_{10}H_7NO_2$.

Chlorodiazobenzenetolylguanidine, $C_6H_4Cl{\cdot}N_2{\cdot}C(NH){\cdot}NH{\cdot}C_7H_7$, is formed by the direct union of chlorodiazobenzene cyanide with paratoluidine in alcoholic solution in presence of a few drops of aqueous soda. It forms reddish-brown crystals melting at 167°. The *hydrochloride* is a coloured, crystalline substance. The diazocyanides also unite with hydrogen chloride to form imidochlorides, which are exceedingly unstable.

Chlorobenzenehydrazocarbamide, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, is obtained by the reduction of chlorobenzenediazocarbamide with alcoholic ammonium sulphide. It forms white crystals, melts at 232°, and reduces ammoniacal silver oxide. *Chlorobenzenehydrazothiocarbamide*, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2$, is obtained by passing hydrogen sulphide into an alcoholic solution of chlorobenzenediazocyanide and melts at 198°.

The compound of diazobenzene cyanide with hydrogen cyanide is converted by reduction into the imidocyanide of benzenehydrazocarboxylic acid, which is identical with Fischer's dicyanophenyl hydrazine. A. H.

Action of Diazo-compounds on Ethylic Cyanacetate. By B. MARQUARDT (*J. pr. Chem.*, 1895, [2], **52**, 160—176; compare Abstr., 1894, i, 369).—The salts previously described as labile forms of azocyanacetates (Abstr., 1894, i, 369) are probably correctly so described, whilst the stable forms are hydrazonecyanacetates. The former can be converted into the latter by heating them above their melting points, or by heating them with alcohol.

Ethylic metabromophenylhydrazonecyanacetate,

$$C_6H_4Br{\cdot}N_2H{:}C(CN){\cdot}COOEt,$$

is prepared by diazotising a solution of bromaniline in glacial acetic acid, adding ethylic cyanacetate, cooling in a freezing mixture, and adding crystalline sodium acetate. It forms yellow crystals, melts at 102°, and dissolves freely in alcohol and ether, but only sparingly in benzene, chloroform, and light petroleum. By dissolving it in alcoholic potash and adding hydrochloric acid to the solution, *ethylic azobromobenzenecyanacetate*, $N_2Ph{\cdot}CH(CN){\cdot}COOEt$, is precipitated; this melts at 153°, and is converted into the phenylhydrazonecyanacetate when heated with alcohol. The isomerides differ from each other in their solubility in benzene, the stable form (m. p. 102°) being six times as soluble as the labile form. When ethylic metabromophenylhydrazonecyanacetate is heated with aqueous potash, it yields

bromophenylhydrazoneacetic acid, which melts at 167° and gives precipitates with solutions of most metallic salts.

Ethylic dibromophenylhydrazonecyanacetate,

$$C_6H_3Br_2\cdot N_2H{:}C(CN)\cdot COOEt,$$

is prepared in a similar manner from dibromaniline [$NH_2 : Br_2 = 1 : 2 : 5$], but the yellow crystals obtained in this way melt at 160°, and appear to be a mixture of the two isomerides, for when they are dissolved in potash, hydrochloric acid precipitates the labile form (*ethylic azodibromobenzenecyanacetate*), which melts at 172°, whilst carbonic anhydride precipitates the stable form (the hydrazonecyanacetate), which melts at 144°. One hundred parts of benzene dissolve 0·6943 part of the labile form and 0·1159 part of the stable form.

Ethylic tribromophenylhydrazonecyanacetate,

$$C_6H_2Br_3\cdot N_2H{:}C(CN)\cdot COOEt,$$

when prepared from tribromaniline ($NH_2 : Br_3 = 1 : 2 : 4 : 6$) by the process described for the monobromo-derivative, crystallises in lustrous, golden laminæ, which melt at 144° and therefore contain a little of the labile isomeride. When these crystals are dissolved in potash, carbonic anhydride precipitates the hydrazonecyanacetate from the solution in crystals, which melt at 141° and dissolve to the extent of 5·103 parts in 100 parts of benzene at 15°. The labile form (*ethylic azotribromobenzenecyanacetate*) is precipitated from the potash solution by hydrochloric acid; it melts at 134°, and dissolves to the extent of 8·852 parts in 100 parts of benzene.

Ethylic α-naphthylhydrazonecyanacetate, $C_{10}H_7\cdot N_2H{:}C(CN)\cdot COOEt$, is prepared from α-naphthylamine by diazotisation and addition of ethylic cyanacetate; it forms yellow-brown crystals, melts at 147°, and dissolves to the extent of 2·3482 parts in 100 parts of benzene. When hydrolysed with alcoholic potash, it yields the corresponding *acid*, which forms dark yellow-brown crystals and melts at 125°. *Ethylic azo-α-naphthalenecyanacetate*, prepared by precipitating the potash solution of the hydrazonecyanacetate with hydrochloric acid, forms brown-red crystals, melts at 105°, and dissolves to the extent of 3·5006 parts in 100 parts of benzene.

Ethylic β-naphthylhydrazonecyanacetate, as first prepared, melts at 142°, but when separated from the labile form by dissolution in potash and precipitation with carbonic anhydride, it melts at 145° and dissolves in benzene to the extent of 2·571 parts in 100 parts. Hydrolysis with alcoholic potash converts it into the corresponding *acid*, which forms granular, yellow crystals and melts at 150°. *Ethylic azo-β-naphthalenecyanacetate* is precipitated from its potash solution by hydrochloric acid; it melts at 124° and dissolves in benzene to the extent of 5·137 parts in 100 parts.

Neither iodine nor sulphurous acid will change the labile form of ethylic tribromophenylhydrazonecyanacetate into the stable form; but a small quantity of iodine will convert the labile form of ethylic α-naphthylhydrazonecyanacetate into the stable form.

Ethylic metacarboxyphenylhydrazonecyanacetate,

$$COOH\cdot C_6H_4\cdot N_2H{:}C(CN)\cdot COOEt,$$

was prepared by diazotising metamidobenzoic acid, adding ethylic cyanacetate, and salting out with sodium acetate; it forms crystals which melt at 222°. An alcoholic solution of the salt gives precipitates with various metallic salts; these are duly described; the *silver* salt was analysed. An isomeride was not obtained.

Ethylic hydroxyphenylhydrazonecyanacetates,

$$OH\cdot C_6H_4\cdot N_2H{:}C(CN)COOEt,$$

were prepared by diazotising the corresponding amidophenols with amyl nitrite and hydrochloric acid, adding ethylic cyanacetate, and salting out with sodium acetate. The *orthohydroxy*-derivative forms dark brownish-yellow crystals and melts at 204°; the *para*-derivative crystallises in yellow needles and melts at 150°; the *meta*-derivative crystallises in dark, red-brown needles and melts at 87°.

Ethylic sulphophenylhydrazonecyanacetate,

$$SO_3H\cdot C_6H_4\cdot N_2H{:}C(CN)\cdot COOEt,$$

prepared from diazobenzenesulphonic acid and ethylic cyanacetate, forms yellow crystals, which decompose before they melt, but without explosion; it dissolves freely in water and in dilute alcohol, but not in absolute alcohol, benzene, ether, or chloroform. A *silver* salt was prepared. A. G. B.

Isomeric Diazo-derivatives. By Heinrich Goldschmidt (*Ber.*, 1895, **28**, 2020—2027).—The author has examined the depression of the freezing point in solutions of isodiazobenzene potassium and of diazobenzene sodium, a solution of the latter being obtained by the addition of diazobenzene chloride to a solution of soda of known strength and freezing point. The results obtained are analogous to those given by the salts of the syn- and anti-aldoxime salts (this vol., i, 657), and confirm Hantzsch's theory, that these diazo-derivatives are stereo-isomerides, similar to the aldoximes, but do not agree with Bamberger's supposition, that the former has the constitution N:NPh·OH, and the latter PhN:N·ONa. In any case, the author regards the first formula as extremely improbable, as the radicle, Ph·N:N, is a substituted ammonium derivative, and it is extremely unlikely that its hydroxide would possess strongly acid properties.

In the latter portion of the paper, the author proposes a theory of the diazo-compounds which is identical with that just published by Hantzsch (this vol., i, 516), namely, that there are two structurally isomeric classes of diazo-compounds, the first containing the radicle, PhN:N, and the second the true diazo-group, Ph·N:N·, and that the latter are, as Hantzsch has long maintained, capable of existing in two stereoisomeric forms. The reasoning on which these conclusions are based is practically identical with that of Hantzsch in the paper quoted. H. G. C.

Action of Halogens and Thiocarbonyl Dichloride on Amidoximes. By Hans Krümmel (*Ber.*, 1895, **28**, 2227—2233; compare Abstr., 1892, 461).—Benzenylhydrazoximidobenzylidene *hydrobromide* separates from a concentrated solution of benzenylamidoxime in

glacial acetic acid when bromine is added in small quantities until the colour is no longer destroyed. It melts at 132°, and when the solution, in water or alcohol, is heated alone or with acids, ammonium bromide and dibenzenylazoxime are formed. The *hydrochloride* is colourless. When excess of bromine is employed in the preparation of the hydrobromide, the *dibromide* of this salt separates as a red powder, which melts at 132°; benzenylhydrazoximidobenzylidene is obtained by treating it with ammonia, and hot alcohol converts it into dibenzenylazoxime.

Parahomobenzenylhydrazoximidoparabromobenzylidene *hydrobromide* is a white, crystalline substance, and melts at 178°; it resembles the foregoing salt in behaviour, and when treated with bromine yields the *dibromide*, which is orange-yellow, and melts at 135°.

Metanitrobenzenylhydrazoximidometanitrobenzylidene *hydrobromide* is colourless, and melts at 158°; hot alcohol converts it into *dimetanitrobenzenylazoxime*, which melts at 138°. The hydrobromide also yields the *dibromide*, which is yellow, and melts at 142°.

Thiocarbonyldibenzenylamidoxime, $CS(O{\cdot}N{:}CPh{\cdot}NH_2)_2$, is obtained by adding thiocarbonyl dichloride to a solution of benzenylamidoxime in benzene; it melts at 96°, and decomposes very readily in solution.

Benzenylazoximethiocarbinol, $CPh\begin{matrix}<\\<\end{matrix}\begin{matrix}N{\cdot}O\\N\end{matrix}\begin{matrix}>\\>\end{matrix}C{\cdot}SH$, is produced when the solution of the foregoing substance in warm alkali is acidified; it forms white crystals, and melts at 131°. The *ethyl* derivative, obtained by digesting the potassium derivative with ethylic iodide, is decomposed by excess of caustic potash, yielding ethylic mercaptan.

Thiocarbonyldiparahomobenzenylamidoxime is colourless, and melts at 115°. *Parahomobenzenylazoximethiocarbinol* crystallises in white needles, and melts at 135°. M. O. F.

Tolyl- and Phenyl-anilidophosphonium Derivatives. By C. A. August Michaelis and Fritz Kuhlmann (*Ber.*, 1895, **28**, 2212—2217).—*Paratolyltrianilidophosphonium chloride*, $C_7H_7{\cdot}PCl(NHPh)_3$, is prepared by heating paratolyltetrachlorophosphine and aniline hydrochloride at about 200°; it is purified by treatment with hydrochloric acid, crystallises in slender, colourless needles, and melts at 245°. The *platinochloride*, $[C_7H_7{\cdot}P(NHPh)_3]_2PtCl_6$, is deposited in lustrous, golden plates. The *hydroxide*, $C_7H_7{\cdot}P(NHPh)_3{\cdot}OH$, obtained by the action of soda on the chloride, is a colourless, crystalline, anhydrous powder, and melts at 240°. The *iodide* and *bromide* crystallise in needles melting at 235° and 238° respectively; the *nitrate* is crystalline, and melts at 180°.

Phenyltrianilidophosphonium chloride, $PPhCl(NHPh)_3$, is prepared in a similar manner to the tolyl-derivative, which it closely resembles, and crystallises in blue tinted needles melting at 250°. The *platinochloride* is deposited in golden, lustrous plates; the *hydroxide* is pulverulent, and melts at 216°; the *bromide* crystallises in colourless, the *iodide* in yellow, needles melting at 235° and 165° respectively; the *nitrate* forms colourless crystals, and melts at 160°.

J. B. T.

Derivatives of Metahydroxybenzaldehyde. By G. WERNER (*Ber.*, 1895, **28**, 1997—2002).—When metahydroxybenzaldehyde is boiled with anhydrous sodium phenylacetate and acetic anhydride, it undergoes condensation, yielding *metahydroxystilbenecarboxylic acid*, $OH{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}COOH$, which crystallises in white, silky needles melting at 142°; its *silver* salt forms concentric aggregates of needles, which become brown in the light; its *calcium* salt, $(C_{15}H_{11}O_3)_2Ca + 2H_2O$, pointed needles; its *barium* salt, $(C_{15}H_{11}O_3)_2Ba + 3H_2O$, well developed prisms, and the *ethylic* salt, $C_{15}H_{11}O_3Et$, feathery crystals melting at 183°. When heated at about 240°, the acid loses carbonic anhydride, forming *metahydroxystilbene*, $OH{\cdot}C_6H_4{\cdot}CH{:}CHPh$, which crystallises in long, thin needles melting at 180°.

With sodium propionate, metahydroxybenzaldehyde yields the corresponding *metahydroxyphenylcrotonic acid*, $OH{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}COOH$, which forms vitreous plates melting at 130°; the *silver* salt, $C_{10}H_9O_3Ag$, is a thick, white precipitate, which becomes pink, and finally black, on exposure to light, and the *zinc* salt, $(C_{10}H_9O_3)_2Zn$, a white, flocculent precipitate. When treated with sodium amalgam and water, the acid is reduced to the corresponding *metahydroxyphenylbutyric acid*,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHMe{\cdot}COOH,$$

which crystallises in fascicular aggregates of spear-shaped needles melting at 63°.

Attempts were made to bring about the condensation of metahydroxybenzaldehyde and succinic and malonic acids, but without success; metethoxybenzaldehyde, however, also undergoes condensation with the sodium salts of fatty acids, yielding analogous products to the hydroxy-derivative. The ethoxy-derivative may be obtained from the aldehyde, either by the action of potash and ethylic iodide, or by heating it with sodium ethylic sulphate and alkali; it is a yellowish oil, of aromatic odour, which boils at 245°, and soon becomes brown. With sodium acetate and acetic anhydride, it yields *ethylmetacoumaric acid*, $OEt{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COOH$, which crystallises in matted needles and melts at 122°; with sodium propionate, it yields *metethoxyphenylcrotonic acid*, $OEt{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}COOH$, which forms long, spear-shaped crystals melting at 80°. H. G. C.

An Isomeric Dichloride of Cinnamic acid. By CARL T. LIEBERMANN and H. FINKENBEINER (*Ber.*, 1895, **28**, 2235—2247; compare Abstr., 1894, i, 335 and 526).—Cinnamic acid dichloride is usually prepared by passing chlorine into carbon bisulphide or carbon tetrachloride containing cinnamic acid in suspension, the operation being carried on in bright sunlight; it melts at 167—168°. A different product is obtained, however, when the following conditions are observed. Cinnamic acid (60 grams), suspended in carbon tetrachloride (750 grams), is submitted to the action of a current of chlorine (31 grams), the liquid being maintained at the temperature of melting ice, and carefully protected from light; after remaining under these conditions for 8—10 days, solution is complete, and the liquid is transferred to vacuum desiccators provided with soda-lime and paraffin. The viscous oil thus obtained is con-

verted into the *cinchonidine* salt, from which the pure *cinnamic acid dichloride*, $C_9H_8Cl_2O_2$, is obtained; it separates in beautiful, rhombic crystals from chloroform to which petroleum has been added; it melts at 84—86°. It is very soluble in chloroform, carbon bisulphide, and carbon tetrachloride; 100 parts of benzene dissolve 43·1 parts at 21°, the same quantity of solvent being required by 2·3 parts of the ordinary dichloride at this temperature. The *methylic* salt is an oil which does not solidify when sown with crystals of methylic cinnamate dichloride (m. p. 100—101°).

The isomeric cinnamic acid dichloride is dissolved by cold ammonia or soda, chlorocinnamene being formed when the liquid is heated; this decomposition is effected more readily than is the case with ordinary cinnamic acid dichloride, and an alkaline solution of potassium permanganate is also attacked more rapidly, benzoic acid being produced.

The removal of the halogen from cinnamic acid dichloride and its isomeride, or from cinnamic dibromide and allocinnamic dibromide, results in the formation of cinnamic acid, whilst methylic cinnamate is obtained from their methylic salts, and from the methylic salt of the so-called allocinnamic acid dichloride.

The following crystallographic information is included in the paper. Cinnamic acid dibromide crystallises in colourless plates belonging to the monosymmetric system; $a : b : c = 0{\cdot}5472 : 1 : 0{\cdot}4894$; $\beta = 88° 34{\cdot}5'$. Cinnamic acid dichloride (m. p. 167—168°) belongs to the monoclinic system; $a : b : c = 0{\cdot}2445 : 1 : 0{\cdot}3485$; $\beta = 77° 59'$. The isomeride forms rhombic crystals; $a : b : c = 0{\cdot}8114 : 1 : 1{\cdot}3611$. The dibromide of methylic cinnamate crystallises in monoclinic plates; $a : b : c = 0{\cdot}91428 : 1 : 1{\cdot}47985$; $\beta = 83° 1'$. The dibromide of the ethylic salt is monosymmetric; $a : b : c = 0{\cdot}5541 : 1 : 0{\cdot}8000$; $\beta = 88° 54'$. The dichloride of methylic cinnamate is isomorphous with the dibromide; $a : b : c = 0{\cdot}89585 : 1 : 1{\cdot}4278$; $\beta = 81° 23{\cdot}5'$.

M. O. F.

Diazosulphanilic acid and its Stereoisomeric Salts. By Arthur Hantzsch and D. Gerilowski (*Ber.*, 1895, **28**, 2002—2012).—This paper contains a detailed account of the investigation of diazosulphanilic acid and its salts, some of the results of which have already been mentioned by Hantzsch, in his recent paper on diazonium compounds (this vol., i, 516). Diazosulphanilic acid has not the constitution usually assigned to it, namely,

$$C_6H_4\langle\begin{matrix}N{:}N\\SO_2\end{matrix}\rangle O,$$

but, like all other diazo-compounds which are stable in acid solution, is in reality a diazonium compound, having the constitution,

$$N{:}N\langle\begin{matrix}C_6H_4\\O\text{—}\end{matrix}\rangle SO_2,$$

and is the neutral anhydride of the diazoniumsulphonic acid. From the molecular weight in aqueous solution, it is shown that the above is the molecular formula.

When diazosulphanilic acid is treated with soda under certain

conditions of concentration and below 0°, it is converted into *sodium syndiazobenzenesulphonate*, $\begin{matrix}N\cdot C_6H_4\cdot SO_3Na\\ \|\\ N\cdot ONa\end{matrix}$, which forms white, silky needles, containing $4H_2O$, $3\frac{1}{2}$ mols. of which are evolved when it is kept over sulphuric acid or phosphoric anhydride; it rapidly reddens on exposure to air, but is perfectly stable if kept over calcium chloride. Its aqueous solution has a strongly alkaline reaction; it unites with alkaline β-naphthol with great readiness, and loses the whole of its nitrogen on warming in a current of carbonic anhydride. It also gives an intense yellow coloration with ammonia, and turns the skin orange, or dark red. When heated quickly with a small quantity of water, it is converted into the stereoisomeric *sodium antidiazobenzenesulphonate*, $\begin{matrix}N\cdot C_6H_4\cdot SO_3Na\\ \|\\ ONa\cdot N\end{matrix}$, already obtained by Bamberger, and supposed by him at first to be a nitrosamine derivative; it forms nacreous plates, contains no water of crystallisation, only gives a slight coloration with β-naphthol, and does not affect the skin. The conversion of the syn- into the anti-salt also takes place slowly at the ordinary temperature in aqueous solution, but the solid syn-salt may be kept many weeks in an exsiccator without alteration. The syn-potassium salt is obtained in the same manner as the sodium salt, and appears to be anhydrous, but gradually changes into the anti-salt, even in the solid state. Both the syn- and anti-salt lose nitrogen when boiled with water, the elimination being complete with the former, and nearly so with the latter.

In order to prove that these two salts are in reality both true diazo-compounds, the degree of dissociation and number of ions in their aqueous solutions was determined, and found to be three in both cases, whereas if either of the salts was a diazonium derivative, the number of ions must have been at least four. Both salts being therefore diazo-compounds, they must be regarded as stereoisomerides.

An indirect proof of the intramolecular change which takes place in the formation of syndiazobenzene salts from diazosulphanilic acid is found in the action of alkalis on the latter. When slightly less than an equivalent of alkali is added to a solution of diazosulphanilic acid, at 0° and quite neutral, the reaction of the mixture becomes strongly alkaline, but after a time the solution gradually becomes neutral again, without any evolution of nitrogen. The first addition of alkali causes the formation of the salt still containing the free diazonium radicle, which has an alkaline reaction, but this gradually undergoes an intramolecular change into the diazo-group forming the neutral salt, $ONa\cdot N{:}N\cdot C_6H_4\cdot SO_3Na$. Conversely, if acid be added to the syn-diazo salt, $ONa\cdot N_2\cdot C_6H_4\cdot SO_3Na$, the solution becomes neutral as soon as it is completely converted into the salt, $OH\cdot N_2\cdot C_6H_4\cdot SO_3Na$; on the further addition of acid, the solution assumes an acid reaction, but after a few minutes again becomes neutral, owing to the formation of the diazonium group, which is the only form capable of existing for any length of time in acid solution. H. G. C.

Diphenacylacetic acid and its Reduction Products. By AUGUST PUSCH (*Ber.*, 1895, **28**, 2102—2106).—The acid obtained by Sattler (Abstr., 1893, i, 389) from chloralacetophenone by treatment with hot sodium carbonate solution is identical with the diphenacylacetic acid prepared by Knes and Paal (*Ber.*, **19**, 3147). On reduction with sodium amalgam, this acid is converted into 3 : 4-*dihydroxydiphenylpentamethylene*-1-*carboxylic acid*, $COOH\cdot CH<\begin{matrix}CH_2\cdot CPh\cdot OH\\ CH_2\cdot CPh\cdot OH\end{matrix}'$ which crystallises in needles, and melts and decomposes at about 200°. This acid, which is insoluble in cold benzene, is accompanied by an isomeric acid, which is readily soluble in benzene, and melts at 162—164°. This second acid is probably an allo-form of that first described. Each of these forms, when heated with hydriodic acid and phosphorus, yields the same two isomeric 3 : 4-*diphenylpentamethylenecarboxylic acids*. One of these crystallises in nodular aggregates, melting at 186—187°, whilst the other, which the author names the *allo-acid*, is remarkably soluble in cold benzene, and melts at 150—152°.

Three stereo-isomerides of the acid in question are possible, and the exact constitution of the two forms which have been obtained has not yet been ascertained. A. H.

A Brominated Bye-product of the Preparation of Diphenacylacetic acid from Bromacetophenone. By AUGUST PUSCH (*Ber.*, 1895, **28**, 2106—2107; compare the foregoing abstract).—The brominated bye-product obtained in the preparation of diphenacylacetic acid from bromacetophenone and ethylic sodiomalonate crystallises in silky needles, melting at 159—160·5°, and has the molecular formula, $C_{18}H_{15}BrO_3$. It appears to contain a keto-carbonyl group, but its constitution has not yet been ascertained. A. H.

Condensation of Orthotoluidine with α-Diketones and with the Salts of α-Ketonic acids. By VICTOR KULISCH (*Monatsh.*, 1895, **16**, 351—357; compare Abstr., 1894, i, 552).—*Benzoylbenzylidenetoluidine*, $C_6H_4Me\cdot N{:}CPhBz$, obtained on condensation of benzile with orthotoluidine, crystallises from ether in beautiful rhombs [$a : b : c = 0{\cdot}45644 : 1 : 0{\cdot}63358$], is readily soluble in benzene, chloroform, and hot water, melts at 103—104°, and is reconverted by acids into its generators. It yields an *oxime*, $C_{21}H_{18}N_2O$, which crystallises in slender, white needles, dissolves readily in alcohol, and melts at 178—180°.

2 : 2′-*Hydroxymethylquinoline*, $C_{10}H_9NO$, obtained on condensation of orthotoluidine with ethylic pyruvate, crystallises from hot alcohol in slender, white needles, melts at 203—205°, has an aromatic odour, and is only sparingly soluble in water. On distillation with zinc-dust, it yields a red oil, which boils at 239—255°, has the odour of quinaldine, and gives a platinochloride, $(C_9NH_6Me)_2,H_2PtCl_6$, which melts at 226—230°. The base is therefore 2 : 2′-hydroxymethylquinoline, which forms a *platinochloride*, melting at 225—228°, a *sulphate*, melting at 86—87°, and a *picrate*, melting at 95—96°.

G. T. M.

Basic Properties of the Rosanilines and their Derivatives. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], **13**, 427—430).—In reply to Prud'homme (this vol., i, 423), the author reiterates the view he has held for the past 15 years as to the constitution of the rosanilines, namely, that they all contain electropositive univalent radicles of the type, $C(C_6H_4\cdot NH_2)_3$, in combination with chlorine, hydroxyl, &c., and that in the dyes themselves these radicles are combined with such electronegative radicles as chlorine, the corresponding carbinols being colourless. The introduction of sulphonic groups into the phenyl radicles has practically no effect on their basic properties. These views are in reality confirmed by Prud'homme's results. JN. W.

Constitution of the Rosanilines. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], **13**, 431—433).—Prud'homme's view that the rosaniline carbonates are ammonium rather than ethereal salts is inconsistent with the adoption of the author's formula, $CCl(C_6H_4\cdot NH_2)_3$, for the hydrochloride. The fact is that the character of the triphenylcarbinol derivatives varies over a very wide range. Triphenylchloromethane, for example, is hydrolysed by cold water, and thus resembles the acid chlorides in character, whereas triamidotriphenylcarbinol is more basic than ammonia. But triphenylcarbinol forms alkylic ethers as stable as the mixed aliphatic ethers, and is thus still distinctly alcoholic in nature, although its basic character is not sufficiently marked to allow of the formation of salts with acids; triamidotriphenylcarbinol, on the other hand, forms both ethers with alkylic radicles, and ethereal salts with acid radicles. Thus even the most acid in character of the rosaniline group is distinctly alcoholic, and Prud'homme's carbonate must be regarded as a true ethereal salt. JN. W.

Corallin and Rosaniline. By CARL ZULKOWSKI (*Monatsh.*, 1895, **16**, 358—403).—Dyes and other organic compounds having a phenolic character may be conveniently purified by precipitating their alkaline solutions with carbonic anhydride. The method answers well for aurin, roseol, and their derivatives, for phenolphthaleïn, and other similarly constituted substances. Corallin, when prepared from pure phenol, contains two dyes in addition to aurin; these have the formulæ $C_{20}H_{16}O_4$ and $C_{22}H_{16}O_5$(?) respectively, and do not appear to be closely related to each other. Corallin thus obtained also contains two substances which are isomeric but they exhibit no tinctorial properties; they contain 1 atom more of oxygen than aurin, have the formula $C_{19}H_{14}O_4$, and may be regarded as α- and β-aurin oxide respectively. When corallin is prepared from phenol containing orthocresol, in addition to the products mentioned above, the following series of compounds may be isolated: $C_{21}H_{20}O_4$, $C_{22}H_{18}O_4$, $C_{20}H_{16}O_4$, $C_{20}H_{10}O_5$; the first of these is roseol, the others have not previously been isolated. On diazotising rosaniline which is free from the para-compound, the substances $C_{25}H_{22}O_4$ (methylroseol) and $C_{23}H_{20}O_4$ may be obtained. G. T. M.

Theory of Dyeing. Distribution of Methylene-Blue between Water and Mercerised Cellulose. By GEORG V. GEORGIEVICS and ERNST LÖWY (*Monatsh.*, 1895, **16**, 345—350).—It has been previously shown (compare Georgievics, this vol., ii, 259) that the expression $\sqrt[x]{\frac{\text{dye remaining in bath}}{\text{dye taken up by fibre}}}$, where x expresses the measure of the affinity of the dye for the fibre, is a constant for most, if not for all, substantive colours. The authors find that the same expression holds good in the distribution of methylene-blue between water, and cellulose which has been treated with caustic soda (mercerised cellulose), and that it is independent of the structure of the cellulose, which may be fibrous, or in the pulverulent form as obtained on adding an acid to a solution of cellulose in ammoniacal cuprous oxide. It appears, moreover, that the quantity of dye taken up at different temperatures depends on the structure of the cellulose in a definite way, and that a far-reaching analogy exists between dyeing and other absorption phenomena. G. T. M.

Isomeric Naphthalene Derivatives. By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1946—1953).—Witt's acetyl-1-naphthol (Abstr., 1888, 486) is shown to have the properties of 2-acetyl-1-naphthol; it yields *ethylic* and *methylic ethers* only with difficulty. The former of these is an oil boiling at about 320°, and yielding a *phenylhydrazone*, which melts at 117°. Acetyl naphthol yields a hydrazine derivative melting at about 165°. With sulphuric acid, it yields 2-*acetyl*-1-*naphthol*-4-*sulphonic acid*, the *barium salt* of which crystallises with $5H_2O$; this acid, when treated with dilute nitric acid, is converted into yellow 4 : 2-*nitroacetyl*-1-*naphthol*, which melts at 157°, and forms a red *phenylhydrazone* melting at 221°. This nitro-compound is reduced by stannous chloride to 4 : 2-*amidoacetyl*-1-*naphthol*, a reddish-brown substance, of which the *platinochloride* and *acetyl derivative*, melting at 107°, were prepared, and which, when treated with bleaching powder, yields yellowish-brown *acetylnaphthaquinone chlorimide* melting at 137°, and, when oxidised with ferric chloride, a yellow *acetylnaphthaquinone*, which melts and decomposes at 78°.

1 : 3-*Naphthylaminesulphonic acid* was prepared from the 1 : 3 : 1′-amidodisulphonic acid by reducing the latter with sodium amalgam or heating it with 75 per cent. sulphuric acid; its *barium salt* crystallises with H_2O; it can be hydrolysed to 1 : 3-naphtholsulphonic acid. When fused with potash, it yields yellow 1 : 3-*amidonaphthol*, which decomposes at 185°, yields a *monacetyl derivative* melting at 179°, and, when heated with strong aqueous ammonia at 150°, is converted into 1 : 3-*naphthylenediamine*. This substance melts at 96°, and its *diacetyl derivative* at 263°; it has not been properly described before, and it is interesting as completing the list of the possible naphthylenediamines, all of which are now well characterised. C. F. B.

Naphthazarin from 1 : 2 : 1′ : 4′-Tetranitronaphthalene (*δ*). By WILHELM WILL (*Ber.*, 1895, **28**, 2234—2235; compare this vol., i, 235 and 477).—When *δ*-tetranitronaphthalene is reduced with tin

and hydrochloric acid, naphthazarin is produced, and at the same time a substance is formed which crystallises in plates with a bronze lustre; probably this compound is amidodiimidonaphthol (*Ber.*, 1878, **11**, 1661). M. O. F.

Preparation of Anhydrous Diazo-Salts. By EMIL KNOEVENAGEL (*Ber.*, 1895, **28**, 2048—2060; compare Abstr., 1891, 54).—By means of the process already described (*loc. cit.*), the author has prepared the following salts. The diazo-sulphates of α-naphthylamine and β-naphthylamine, the diazo-chlorides of orthotoluidine, α-naphthylamine, and β-naphthylamine, the diazo-nitrates of paranisidine, α-naphthylamine, and β-naphthylamine, and the diazo-oxalates of aniline, paratoluidine, paranisidine, and paraphenetidine. Further particulars are also given regarding those salts which have already been obtained in the anhydrous state (*loc. cit.*). M. O. F.

Note by Abstractor.—Anhydrous β-diazonaphthalene chloride was prepared by Möhlau and Berger (*Ber.*, 1893, **26**, 2000).

Thionylamines of Amidazo-derivatives and of Naphthylenediamines. By C. A. AUGUST MICHAELIS and G. ERDMANN (*Ber.*, 1885, **28**, 2192—2204).—*Thionylparazorthoamidotoluene*,

$$C_7H_7\cdot N{:}N\cdot C_7H_6N{:}SO,$$

is prepared from parazorthoamidotoluene hydrochloride [Me : N = 1 : 2; NH_2 : Me : N = 1 : 2 : 4] and thionylic chloride, in benzene solution; it crystallises in golden needles, melts at 89°, evolves sulphurous anhydride in moist air, is slowly decomposed when boiled with water or alcohol, more rapidly with acids, and immediately with alkalis. All these solutions colour the skin intensely yellow. The isomeric compound from parazorthoparamidotoluene hydrochloride, [Me : N = 1 : 4; NH_2 : Me : N = 1 : 2 : 4] melts at 86°, and is deposited from benzene in small, steel-blue needles, from light petroleum in broad needles with a light bluish-brown lustre. In its properties, it resembles the preceding compound.

Benzeneparazonaphthylamine, $NH_2\cdot C_{10}H_6\cdot N{:}NPh$ [NH_2 : N = 1 : 4], has been previously prepared by Griess; Bamberger and Schieffelin described the hydrochloride under this name; it melts at 123°, and gives bluish-red solutions which become pure red with acids and yellow with alkalis. The *acetyl* derivative crystallises in yellow plates, and melts at 233°. The *benzoyl* derivative forms brownish needles melting at 201°. The free base readily yields a *thionyl* derivative, but the hydrochloride reacts less easily; it crystallises in dark orange-red needles, melts at 136°, and resembles the above toluene compounds.

Thionyl-α-naphthylazo-α-naphthylamine, $C_{10}H_7\cdot \overset{1}{N}{:}\overset{4}{N}\cdot C_{10}H_6\cdot \overset{1}{N}{:}SO$, prepared from the corresponding naphthylnaphthylamine, is brown and pulverulent, and melts at 156—157°. *Thionylorthoazoparamidotoluene*, [N : NSO = 1 : 2], is prepared from the amide, and is deposited in brownish-red crystals melting at 95—105°. It is somewhat unstable, and when heated at 170° (30 mm.) is resolved into the pseudoazimide,

$C_7H_6<\overset{N}{\underset{N}{|}}>NC_7H_7$, sulphur and sulphurous anhydride. This reaction indicates that orthoazamidotoluene is not a closed chain or quinoïdal compound, but has the ordinary open chain formula.

By the interaction of thionylic chloride and benzeneorthoazo-β-naphthylamine, benzenepseudoazimidonaphthylene, sulphur, sulphurous anhydride, and, in small quantity, impure thionylamine are formed. *Naphthalenepseudoazimidonaphthalene*, $C_{10}H_6<\overset{N}{\underset{N}{|}}>N,C_{10}H_7$ [N : N = 1 : 2; N = 2], is formed, when thionylic chloride reacts with β-naphthylorthoazo-β-naphthylamine; it crystallises in colourless needles, and melts at 186°. No thionyl derivative could be obtained.

1 : 4-*Thionylnaphthylenediamine*, $C_{10}H_6(N{:}SO)_2$, prepared from thionylic chloride and naphthylenediamine hydrochloride, crystallises in lustrous, light-brown needles, and melts at 126°; it is slowly decomposed when boiled with water or alcohol, more rapidly by the addition of acids, and immediately by alkalis. Thionylic chloride and orthonapthylenediamine yield naphthylpiazthiole, $C_{10}H_6<\overset{N}{\underset{N}{|}}\gg S$.

J. B. T.

Para-substituted Derivatives of α-Naphthoic acid. By Paul Friedlaender and J. Weisberg (*Ber.*, 1895, **28**, 1838—1843).—The following substances were prepared in the course of an unsuccessful attempt to obtain an anhydride of tetrahydroparamidonaphthoic acid. 1 : 4-*Nitronaphthonitrile*, prepared from nitronaphthylamine by means of the diazo-reaction, crystallises in colourless needles which melt at 133° and are free from odour. The corresponding *amidonaphthonitrile* melts at 174°, is odourless, and forms crystalline salts. The *acetyl* derivative forms needles melting at 189·5°. 1 : 4-*Chloronaphthonitrile*, prepared from the amido-compound by Sandmeyer's reaction, crystallises in long white needles melting at 110°. *Nitronaphthamide*, $NO_2{\cdot}C_{10}H_6{\cdot}CO{\cdot}NH_2$, prepared by the action of hydrogen peroxide on the nitrile in the presence of alcoholic potash (Radziszewski's method), melts at 218°. Both the nitrile itself and the amide are very stable to the ordinary hydrolytic reagents, but may be converted into the acid by boiling aqueous baryta. 1 : 4-*Nitronaphthoic acid* forms faintly yellow needles melting at 220°; it is sparingly soluble in hot water, and forms soluble salts of the alkali metals. The *ethylic salt* crystallises in yellow needles, and melts at 54°. *Amidonaphthamide* forms white needles, which melt at 175°, after previously undergoing decomposition; it is easily decomposed by acids with formation of napthylamine, but is converted by alcoholic potash at 130—140° into *amidonaphthoic acid*. This acid is, however, best prepared by the reduction of nitronaphthoic acid; it is moderately soluble in hot water, and forms brownish needles melting at 177°. It readily decomposes when dissolved in hydrochloric acid, carbonic anhydride being evolved and naphthylamine formed when the liquid is allowed to remain. 1 : 4-*Chloronaphthoic acid* crystallises in white needles, melting at 210°; it is not acted on by ammonia at 200°, or by ammonium carbonate at 220°.

A. H.

Analyses of Cotton Dyed with Alizarin. By CARL T. LIEBERMANN and PAUL MICHAELIS (*Ber.*, 1895, **28**, 2264—2265; compare this vol., i, 108).—The authors give analyses of samples dyed with dark Krapp-red, dark violet, and dark claret; the dyeing being continued, in each case, until the deepest shade was attained. It was found that the proportion of dye to mordant was considerably greater than in all previous cases, thus indicating that the whole of the mordant was dyed. J. J. S.

Derivatives of Anthracene-β-sulphonic acid and Anthracyl Hydrosulphide. By WERNER HEFFTER (*Ber.*, 1895, **28**, 2258—2264).—*Anthracene-β-sulphonic chloride*, $C_{14}H_9 \cdot SO_2Cl$, obtained by heating an intimate mixture of the sodium salt and phosphorus pentachloride with equal parts of phosphorus oxychloride and acetic acid, melts at 122°, and is very stable in the presence of cold water. When oxidised with chromic acid, it yields anthraquinonesulphonic chloride. The *amide*, $C_{14}H_9 \cdot SO_2NH_2$, melts at 261°, is insoluble in ether, alcohol, acetic acid, and benzene, but is soluble in nitrobenzene and in phenol. The *anilide* forms glistening plates, which melt at 201°. The *dimethylanilide*, obtained by acting on the chloride with dimethylaniline, melts at 165°. The *phenylhydrazide*, $C_{14}H_9SO_2NH \cdot NHPh$, melts at 210°.

Tetrabromanthracenesulphonic chloride is obtained by the action of bromine vapour on the chloride; it is a greenish-yellow powder, melts at 125°, and is readily soluble in benzene, acetic acid, and chloroform.

Sodium tetrabromanthracenesulphonate, $C_{14}H_5Br_4 \cdot SO_3Na + 4H_2O$, is a yellow powder readily soluble in warm water.

Methylic anthracenesulphonate, prepared by Krafft and Roos' method (*Ber.*, **25**, 2255, and **26**, 2823), forms yellow plates, melts at 157°, and dissolves in alcohol, ether, and benzene to a blue fluorescent solution. The *ethylic salt* melts at 160°.

Methylic anthraquinonesulphonate, $C_{14}H_7O_2 \cdot SO_3Me$, melts at 123°, and is converted by water or alcohol into the acid. The corresponding *ethylic salt* melts at 125°.

Anthracenesulphinic acid, $C_{14}H_9 \cdot SO_2H$, prepared by acting on the sulphonic chloride with zinc and water, or sodium sulphite, forms greenish plates. The *silver salt* is obtained as a white, flocculent precipitate.

β-Anthracyl hydrosulphide, $C_{14}H_9 \cdot SH$, may be prepared by the methods of Vogt (*Annalen*, **119**, 142), Schiller (*Ber.*, **10**, 939), and Märker (*Annalen*, **136**, 78). It crystallises from benzene in pale yellow needles, decomposes at 220°, and is odourless. The *mercurochloride* compound forms a canary-yellow precipitate, which is decomposed by warm hydrochloric acid into the mercaptan and mercuric chloride. J. J. S.

Diphenylanthrone. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1895, **121**, 102—106).—When the phthalic tetrachloride melting at 88° is dissolved in four parts of benzene free from thiophen, and mixed with 3·5 parts of dry aluminium chloride, the

temperature being kept at 40°, it yields *diphenylanthrone*. With other proportions of aluminium chloride, phenyloxanthranol and anthraquinone are formed. It follows from the production of these compounds that, unless molecular transpositions are assumed to take place, the phthalic tetrachloride melting at 88° is unsymmetrical, and has the constitution $CCl_3 \cdot C_6H_4 \cdot COCl$.

Diphenylanthrone is also obtained by the condensation of benzene with phenyloxanthranol in presence of sulphuric acid, and is probably identical with the product obtained by Baeyer under these conditions, but not described by him; it is also formed by the action of benzene and aluminium chloride on *phenyloxanthranol chloride*. The latter is obtained by heating at 140—150° a mixture of diphenylphthalide and phosphorus pentachloride in molecular proportion, and crystallises in white prisms melting at 164° (uncorr.).

Diphenylanthrone can also be obtained by the action of benzene and aluminium chloride on anthraquinone dichloride (dichloranthrone). There would seem to be no doubt that its constitution is $CPh_2<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CO$. Whatever the mode of formation, it crystallises in colourless, very brilliant needles melting at 192°, insoluble in water and almost insoluble in alcohol, ether, or light petroleum, but soluble in boiling benzene or glacial acetic acid. Cryometric determinations show that its molecular weight is 346. Notwithstanding the presence of the CO-group, it combines neither with hydroxylamine nor with phenylhydrazine. C. H. B.

Isomerism in the Terpene Series. By Otto Wallach (*Ber.*, 1895, **28**, 1955—1967).—The study of carvenone and isothujone has been repeated, and the results agree with those obtained earlier (*Annalen*, **286**, 102). The ketones studied were isolated by means of their semicarbazide compounds (compare Baeyer, this vol., i, 536); the latter were usually obtained in two modifications with different melting points; that melting at the higher temperature being referred to as the α-modification. The substances described were all obtained in a very pure state; their physical constants are enumerated below, d standing for specific gravity, n_D for index of refraction, and M for molecular refraction.

Melting-points of	Semicarbazone.		Oxime.
	α.	β.	
Isothujone	208—209°	184—185°	119—120°
Carvotanacetone	177—178	—	92—93
Carvenone	200—201	153—154	91°
Thujamenthone	179°	—	95—96°
Tetrahydrocarvone	173—174°	135—140?	105°

		Boiling-point.	d.	n_D.	M.
$C_{10}H_{16}O$.	Thujone	200—201°	0·917	1·4511	44·61
	Dihydrocarvone	221—222	0·927	1·4717	45·84
	Carvenone	232—233	0·927	1·4822	46·76
	Isothujone	231—232	0·927	1·4822	46·76
	Carvotanacetone	228—229	0·932	1·4793	46·27
	Pulegone	221—222	0·936	1·4846	46·51
$C_{10}H_{18}O$.	Tetrahydrocarvone (dihydrocarvenone)	220—221°	0·904	1·4554	46·55
	Thujamenthone	208—209	0·891	1·4471	46·19
	Menthone	208°	0·894	1·4496	46·25

The calculated values of M are as follows (a double linking being denoted by $|^{=}$).

Ketone, $C_{10}H_{16}O$.	Alcohol, $C_{10}H_{15}\cdot OH|^{=}$.	Ketone, $C_{10}H_{16}O|^{=}$.	Alcohol, $C_{10}H_{15}\cdot OH|^{=2}$.	Ketone, $C_{10}H_{18}O$.
44·11	45·05	45·82	46·76	46·21

Dihydrocarvone has the physical characters of an unsaturated, thujone that of a saturated, ketone. When treated with dilute sulphuric acid, they are converted into isomeric substances, carvenone and isothujone respectively; these have an identical physical character—that of an alcohol with two ethylene linkings, but their chemical character is that of a ketone with one ethylene linking; an anomaly of the same kind is exhibited by pulegone. Carvenone and isothujone are converted by reduction into the alcohols tetrahydrocarveol and thujamenthol, $C_{10}H_{20}O$, and these, on oxidation, yield tetrahydrocarvone and thujamenthone.

Thujone (tanacetone) is further converted at 280° into carvotanacetone; this already differs from isothujone, and when it is reduced to a tetrahydro-derivative (alcohol), and the latter is oxidised, a substance is obtained which is identical with tetrahydrocarvone, and different from thujamenthone. Thujone is thus converted by heat into a different isomeride from that into which dilute sulphuric acid transforms it. C. F. B.

Alcohols derived from a Dextro-rotatory Terpene, Eucalyptene. By Gustave Bouchardat and Tardy (*Compt. rend.*, 1895, **120**, 1417—1420).—Eucalyptene, the dextrogyrate terpene of eucalyptus, has a specific rotatory power of $[\alpha]_D = +39$ at 15°; in boiling point (156—157°) and sp. gr. (0·870 at 0° and 0·865 at 18°), it is identical with the lævogyrate terpene from the pine oil of Landes. When heated with glacial formic acid, it yields a terpilenol, $C_{20}H_{18}O_2$, which has a peculiar odour of lilac, crystallises from ether in bulky crystals melting at 33—34°, boils and decomposes at about 218°, and otherwise resembles the terpilenol from the lævogyrate terpene, but its specific rotatory power $[\alpha]_D = +88°$.

When heated with benzoic acid at 150°, eucalyptene yields a

borneol which melts and boils at about 213°. Its rotatory power $[\alpha]_D = +18° 40'$, whilst that of the corresponding camphor is +31°, and hence the ratio between the two is abnormal, and indicates the presence of the isomeride with reversible rotatory power described by Montgolfier. In fact, by repeated conversion into the benzoate, the specific rotatory power of the borneol can be raised to +25° 50′, whilst that of the camphor formed from it remains constant at +31°. The camphor, when oxidised with nitric acid, yields a mixture of ordinary camphoric acid, which is somewhat soluble in water, melts at 181°, and has a specific rotatory power of +44°, and racemocamphoric acid which is only slightly soluble in water, melts at 203—204°, and yields an anhydride which melts at 223°. The borneol seems consequently to be a mixture of dextrogyrate borneol with some normal lævogyrate borneol and the lævogyrate borneol of Montgolfier, with variable rotatory power.

The isoborneol or fenchol, $C_{10}H_{14}O_2$, obtained at the same time as the borneol melts at about 45°, boils at 198—200°, and has all the properties of the isoborneol from the lævogyrate terpene, except that its specific rotatory power is −10° to −10° 20′. The corresponding camphor is strongly dextrogyrate, liquid at 15°, and solid at 0°, and seems to be identical with the anisic camphor of Landolph or the fenchone of Wallach.

The inactive eucalyptene seems to be a true racemic hydrocarbon; it yields racemic borneol, inactive camphor, racemic camphoric acid melting at 203—204°, and the racemic camphoric anhydride melting at 223°. It also yields an inactive isoborneol, a liquid racemic camphor, and an inactive terpinol, which seems to be identical with the terpinol from terpin. C. H. B.

Oxidation of Dihydrocarveol and of Limonene. By Ferdinand Tiemann and Friedrich W. Semmler (*Ber.*, 1895, **28**, 2141—2150).—By treating the trihydroxyhexahydrocymene, obtained by the oxidation of dihydrocarveol (Wallach, *Annalen*, **277**, 151), with a mixture of chromic anhydride and sulphuric acid, the authors have obtained a substance which, from its reactions, they consider to be 3 : 1 : 6-*acetylhydroxymethylhexamethylene*,

$$CHMe\begin{<}CH_2 \text{——} CH_2\\ CH(OH)\cdot CH_2\end{>}CH\cdot COMe.$$

It is an oil which distils at 155—156° under a pressure of 22 mm., and apparently yields a mixture of two oximes, one of which melts at 128°. When treated with an alkaline solution of bromine, it gives *metahydroxyhexahydroparatoluic acid*; this melts at 153°, decomposes sodium carbonate, yields a sparingly soluble silver salt, and a phenylurethane derivative which melts at 193—194°. When treated with bromine at 190°, the acid is converted into a mixture of metahydroxyparatoluic acid and paratoluic acid. The authors think that these facts point to the following constitutions.

Trihydroxyhexahydrocymene from dihydrocarveol,

$$CHMe\begin{<}CH_2 \text{——} CH_2\\ CH(OH)\cdot CH_2\end{>}CH\cdot CMe(OH)\cdot CH_2\cdot OH.$$

Dihydrocarveol, $CHMe<\begin{matrix}CH_2 \text{---} CH_2\\ CH(OH)\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2$. Carvone, $CMe<\begin{matrix}CH\cdot CH_2\\ CO\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2$. Limonene,

$$CMe<\begin{matrix}CH\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2.$$

All these substances are optically active, and contain an asymmetric carbon atom.

Dihydrocarvone, when treated according to Wagner's method, and then further oxidised with chromic anhydride, yields a diketone, $CHMe<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot CH_2\end{matrix}>CH\cdot COMe$, which distils at 152—160° under a pressure of 22 mm. It yields two isomeric *dioximes*, one of which melts at 197—198°, and the other at 175—176°.

The authors give constitutional formulæ for the products obtained by Best (Abstr., 1894, i, 361) and by Wallach (Abstr., 1894, i, 421) on the oxidation of carvone. Hydroxyterpenylic acid has the constitution $\begin{matrix}COO\cdot CMe\cdot CH_2\cdot OH\\ CH_2\text{–}CH\cdot CH_2\cdot COOH\end{matrix}$, and the $\gamma\delta$-lactone the constitution

$$\begin{matrix}COO\cdot CMe\cdot CH_2\cdot O\\ CH\text{–}CH\text{—}CH_2\cdot CO\end{matrix}$$

Oxidation experiments with limonene are being continued; the results already obtained agree with the formula for limonene given above.

J. J. S.

Optically Active Terpineol. By Friedrich W. Semmler (*Ber.*, 1895, **28**, 2189—2191).—By the substitution of hydroxyl for chlorine, limonene hydrochloride is converted into active *terpineol*,

$$OH\cdot CMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH\end{matrix}>CMe,$$

which boils at 215°, and has an odour of hawthorn blossom and lilac; its optical activity is of the same sign as that of the limonene derivative.

J. B. T.

Bromophenylhydrazone and Semicarbazone of d-Camphor. By Ferdinand Tiemann (*Ber.*, 1895, **28**, 2191—2192).—d-*Camphor-parabromophenylhydrazone*, $C_{10}H_{16}{:}N\cdot NH\cdot C_6H_4Br$, is prepared by the interaction of camphor and parabromophenylhydrazine in concentrated acetic acid solution, at the ordinary temperature; it crystallises in pale yellow plates, melts at 101°, and gradually darkens on exposure to air. The corresponding *semicarbazone*, $C_{10}H_{16}{:}N\cdot NH\cdot CO\cdot NH_2$, forms colourless needles melting at 236—238°.

J. B. T.

Campholene Derivatives. By Ferdinand Tiemann (*Ber.*, 1895, **28**, 2166—2189).—The formulæ previously assigned to a number of campholene derivatives (this vol., i, 426) require amendment in respect to the position of the ethylene linking, the formulæ given for the α-compounds are actually those of the β-series, and *vice versâ*.

α-Campholenonitrile is converted into β-campholenonitrile by the prolonged action of strong acids, hydriodic acid acting the most readily. *d*-Camphoroxime, however, may be recrystallised from moderately concentrated hydrochloric acid without change.

α-Campholenamide, $NH_2\cdot CO\cdot CH_2\cdot CH<\begin{matrix}CH_2-CH\\ \|\\ CMe_2\cdot CMe\end{matrix}$, is formed when the nitrile is hydrolysed by alcoholic potash or when it is fused with potassium hydroxide; it is also obtained by the dehydration of ammonium α-campholenate; it readily crystallises, melts at 130°, is lævogyrate, and is converted into β-campholenamide by the action of mineral acids. Isoamidocamphor is formed by the action of mineral acids on either of the nitriles or amides, but when these are hydrolysed by means of alcoholic potash, α- and β-campholenic acids are obtained; the former is an oil, and boils at 251—255° under atmospheric pressure, and at 142—144° at 10 mm.; β-campholenic acid boils at 245°.

Dihydrocampholenolactone boils at about 260°; when quite free from campholenic acids, it may be distilled under reduced pressure without decomposition, it then crystallises, and melts at 25—30°; the lactone is best freed from the acids by repeatedly treating it, in ethereal solution, with ammonia. Isohydroxycamphor, $CH<\begin{matrix}CH_2\text{——}CO\\ \text{——}CH_2\text{——}\\ CMe_2\cdot CHMe\end{matrix}>C\cdot OH$, is probably formed in traces when the lactone is heated under reduced pressure, but only the lactone could be obtained by the interaction of isoamidocamphor hydrochloride and sodium nitrite. Béhal's optically active dihydrocampholenolactone, prepared from α-campholenamide hydriodide, probably contains α-campholenic acid.

Hydroxydihydrocampholenic acid may be boiled with potassium permanganate without decomposition; at higher temperatures, a part of the acid is oxidised to acetic acid, carbonic anhydride, &c. When α-campholenic acid is oxidised at low temperatures with the calculated quantity of dilute potassium permanganate solution, *α-anti*-dihydroxydihydrocampholenic acid, $COOH\cdot CH_2\cdot CH<\begin{matrix}CH_2-CH\cdot OH\\ |\\ CMe_2\cdot CMe\cdot OH\end{matrix}$ (m. p. 144°), and *pinonic acid*, $COOH\cdot CH_2\cdot CH<\begin{matrix}CH_2-CO\\ |\\ CMe_2\cdot CHMe\end{matrix}$, are formed. The former is dextrogyrate, and readily yields a hydroxylactone; when oxidised with chromic acid, it gives isoketocamphoric acid (this vol., i, 478), and when cautiously treated with nitric acid is converted into *isodiketocamphoric acid*,

$$COMe\cdot CMe_2\cdot CH(CH_2\cdot COOH)\cdot CO\cdot COOH,$$

the constitution of which has not yet been absolutely proved. Dihydrocampholenolactone and α- and β-campholenic acids, when carefully oxidised with chromic acid, in presence of sulphuric acid, yield *hydroxydihydrocampholenolactone*,

$$CH<\begin{matrix}CH_2\text{——}CO\cdot O\\ \text{——}CH_2\text{——}\\ CMe_2\cdot CMe(OH)\end{matrix}>CH,$$

melting at 144°. *α-Syndihydroxydihydrocampholenic acid*,

$$COOH\cdot CH_2\cdot CH<\begin{matrix}CH_2-CH\cdot OH\\ |\\ CMe_2\cdot CMe\cdot OH\end{matrix}$$

melts at 91°, and readily regenerates the lactone, from which it is formed by the action of alkalis. When further oxidised with chromic acid, both hydroxydihydrocampholenolactone and dihydrocampholenolactone yield isoketocamphoric acid, isocamphoronic acid, and terebic acid. It is the study of these reactions that has led the author to revise his previous views on the position of the ethylene linking in the α- and β-campholene derivatives (see above). β-Campholenic acid, when oxidised with dilute solution of potassium permanganate, yields *β-dihydroxydihydrocampholenic acid*, which is optically inactive, and melts at 146°, and an acid which probably has the formula $COOH\cdot CH_2\cdot CH<\begin{matrix}CO—CH_2\\ CMe_2\cdot CHMe\end{matrix}$; it boils 40—50° lower than pinonic acid, with which it is isomeric. β-Dihydroxydihydrocampholenic acid, when oxidised with chromic acid, is converted into oxalic acid, and *acetyldimethylbutyric acid*,

$$COMe\cdot CMe_2\cdot CH_2\cdot CH_2\cdot COOH,$$

which is crystalline, melts at 48—49°, and by the action of alkaline bromine solution yields dimethylglutaric acid (m. p. 85°); this, when oxidised with nitric acid, gives unsymmetrical dimethylsuccinic acid.

Béhal and Blaise's recent investigation of the nitrosocampholene derivatives (*Compt. rend.*, **121**, 258) is discussed. According to the author's view, nitrosocampholenic acid (m. p. 134·5°) and nitrosodihydrocampholenolactone have the formulæ

$$COOH\cdot CH_2\cdot CH<\begin{matrix}CH:CH\\ CMe_2\cdot CMe\cdot NO\end{matrix} \quad \text{and} \quad CH<\begin{matrix}CH_2 —— COO\\ CH_2\\ CMe_2\cdot CMe(NO)\end{matrix}>CH$$

respectively; the ketonic acid (m. p. 126°) is probably either stereoisomeric with pinonic acid, or formed from a γ-lactone into which a portion of the original δ-derivative may have been converted. In support of this, it is stated that dihydrocampholenolactone (b. p. 260°), which is certainly a δ-compound, yields an isomeric lactone, which boils at 230—240°, and is probably a γ-compound; both give the same acid when hydrolysed. The preceding results are fully discussed, and shown to be in complete agreement with the formulæ for camphor, camphoric acid, and the campholenic acids given above, and in the previous communication. The production of campholene from β-campholenic acid and sodium hydroxide is probably preceded by the formation of a hydroxydihydrocampholenic acid, $COOH\cdot CH_2\cdot C(OH)<\begin{matrix}CH_2—CH_2\\ CMe_2\cdot CHMe\end{matrix}$, which should yield one or other of the hydrocarbons, $CMe<\begin{matrix}CH—CH_2\\ CMe_2\cdot CHMe\end{matrix}$, $CH_2{:}C<\begin{matrix}CH_2-C\ H\\ CMe_2\cdot CHMe\end{matrix}$. This subject is under investigation. Béhal has objected to the author's camphor formula on the ground of its inadequacy to explain the production of 1 : 2 : 4-trimethylbenzene from campholic acid; as stated in the previous communication, the

conversion of terpenes into benzene derivatives is extremely complex and preceded by the formation of intermediate compounds, which are usually unstable. The subject will be dealt with more fully subsequently. J. B. T.

Oxidation and Nitration of Benzylidenecamphor and Benzylcamphor. By ALBIN HALLER (*Compt. rend.*, 1895, **121**, 35—38).—When a solution of benzylidenecamphor in glacial acetic acid is heated at 100° with fuming nitric acid, it yields a compound, $C_{17}H_{18}N_2O_5$, which crystallises in white plates melting at 183°, only slightly soluble in hot alcohol, and soluble in boiling benzene. It is not affected by sodium carbonate solution, and when reduced with tin and hydrochloric acid, it yields the original benzylidenecamphor. It seems to be analogous to the compound obtained by Guthrie from amylene (*Annalen*, **116**, 284, and **119**, 84), or to those obtained by Gabriel from benzylidenephthalide (Abstr., 1885, 902), and probably has the constitution $C_8H_{14}<\begin{matrix}C(NO_2)\cdot CHPh\cdot NO_2\\ |\\ O\end{matrix}$. This view is supported by the fact that the same compound is formed when a solution of benzylidenecamphor in glacial acetic acid is gently heated with amylic nitrite and fuming nitric acid.

The prolonged action of hot nitric acid on benzylidenecamphor yields a mixture of camphoric and paranitrobenzoic acids. When oxidised with potassium permanganate, it yields camphoric and benzoic acids.

Benzylcamphor does not yield a nitro-derivative when heated with fuming nitric acid in presence of glacial acetic acid, but prolonged action of hot nitric acid converts it into camphoric and paranitrobenzoic acids, with small quantities of other acids. When oxidised with potassium permanganate, it yields camphoric and benzoic acids.

C. H. B.

Oxidation of Camphoric acid. By FRIEDRICH MAHLA and FERDINAND TIEMANN (*Ber.*, 1895, **28**, 2151—2165; compare this vol., i, 426).—The authors mention the work of Wreden (*Annalen*, **163**, 133), Roser (Abstr., 1886, 249), Balbiano (Abstr., 1894, i, 614), Hlasiwetz and Grabowski (*Annalen*,, **145**, 212), Kachler (Abstr., 1874, 154), Koenigs (Abstr., 1894, i, 46), and Bredt (Abstr., 1894, i, 141 and 613). It is shown that when *d*-camphoric acid is fused with $7\frac{1}{2}$ times its weight of potassium hydroxide for 20—40 minutes at a temperature above 400°, the main products are acetic, isobutyric, pimelic (isopropylsuccinic), *d*-cis- and *d*-cistrans-camphoric acids. The authors have succeeded in separating each of these acids, and consider that the hydroxycamphoric acid of Hlasiwetz and Grabowski is merely a mixture of the pimelic and the cis- and citrans-camphoric acids.

Experiments have been made by treating, with chromic acid mixture, mixtures of propionic and hydroxyisobutyric acids, and of lactic and isobutyric acids, as well as mixtures of their ethereal salts, in order to determine whether trimethylsuccinic acid could be synthesised under such conditions. As their experiments gave negative results, the authors conclude that the trimethylsuccinic acid, obtained by Bredt on oxidising camphoric acid with chromic acid mixture, is a

simple oxidation product of the camphoric acid molecule, and is not the result of a condensation of several simpler oxidation products. They therefore agree with Bredt that the molecules of camphoronic acid, camphoric acid and camphor must contain the grouping C·CMe$_2$·CHMe·C.

The authors also confirm Balbiano's observations on the oxidation of camphoric acid with potassium permanganate (Abstr., 1894, i, 614, and this vol., i, 552). They regard the acid, $C_8H_{12}O_5$, which melts at 120°, as a ketonic dicarboxylic acid of the constitution

COOH·CHMe·CMe$_2$·CO·COOH,

and not as a hydroxydicarboxylic acid. It yields an *oxime* and a *bromophenylhydrazone*, the latter melting at 161—162°. When heated at 170—220°, the acid loses water and carbonic oxide, and is converted into trimethylsuccinic anhydride; when reduced with hydriodic acid and phosphorous, it yields the acids $C_8H_{12}O_4$ and $C_8H_{14}O_4$, which the authors represent as CHMe$<^{CMe_2}_{COO}>$CH·COOH and COOH·CHMe·CMe$_2$·CH$_2$·COOH respectively.

The acid $C_8H_{14}O_4$, when further oxidised, yields unsymmetrical dimethylsuccinic acid.

The acetyl, CHMe$<^{CMe_2}_{COO}>$C(OAc)·COOH, and benzoyl derivatives of the acid melting at 120°, have been previously described by Balbiano.

Camphoronic acid is represented as COOH·CHMe·CMe$_2$·CH(COOH)$_2$, and the authors think that this formula readily accounts for the decomposition of the acid into carbon, carbonic anhydride, trimethylsuccinic acid, and isobutyric acid (compare Bredt, *loc. cit.*).

It is thought that all these facts point to the formulæ recently suggested by Tiemann (this vol., i, 428) for camphor and camphoric acid. Corresponding formulæ for camphanic acid, campholactone, and lauronolic acid are also given. J. J. S.

Action of Phenylic Isocyanate on Campholic, Camphocarboxylic, and Phthalic acids. By Albin Haller (*Compt. rend.*, 1895, **120**, 1326—1329).—Campholic acid, when heated with phenylic isocyanate at a temperature not exceeding 100°, yields campholic anhydride identical with that obtained by Guerbet by the action of acetic anhydride, but at 150—160° the products are (together with carbonic anhydride) aniline and campholanilide, which melts at 90—91°. Attempts to obtain from campholic acid a phenylurethane analogous to that of benzoïn were unsuccessful. It follows that, in its reactions with phenylic isocyanate, campholic acid resembles monocarboxylic acids such as benzoic and toluic acids.

Camphocarboxylic acid, when heated with phenylic isocyanate at 150—170°, yields the dianilide, $C_8H_{14}(CO·NHPh)_2$, which crystallises from chloroform in white needles melting at 222—223°, and from boiling alcohol in elongated, bevelled lamellæ; it is only slightly soluble in cold alcohol, and insoluble in light petroleum. When heated with concentrated alcoholic potash, the dianilide yields

anilidocamphocarboxylic acid, $NHPh\cdot CO\cdot C_8H_{14}\cdot CH_2\cdot COOH$, melting at 203°.

Isophthalic acid heated with phenylic isocyanate at 150—160° yields isophthalic dianilide, which crystallises from acetic acid in white needles melting at about 250°, but is insoluble in most other solvents. Terephthalic acid does not react with the isocyanate even at 210°.

C. H. B.

Vesicating Constituent of Croton Oil. By WYNDHAM R. DUNSTAN and LUCY E. BOOLE (*Proc. Roy. Soc.*, 1895, **58**, 238—240).—The authors have examined the vesicating preparation known as crotonoleïc acid prepared from croton oil by the method directed by Kobert and Hirscheydt. The lead salt was submitted to a process of fractional precipitation by adding successive quantities of water to its solution in alcohol; by this means crotonoleïc acid was proved to be a mixture of inactive oily acids, the lead salts of which are precipitated first, and the true vesicating constituent; the latter, or its lead salt, is principally contained in the last fractions, and represents only a small proportion of the original material.

On saponifying that part of croton oil which is soluble in strong alcohol with a mixture of lead oxide and water and fractionating an alcoholic solution of the lead salts with water, the later fractions, which possessed the greatest vesicating power, furnished a resinous substance having extraordinary power as a vesicant. The authors propose to call it "*croton-resin*." It has the composition $C_{13}H_{18}O_4$, cannot be obtained crystalline, and does not yield any crystalline derivatives. It is a hard, pale yellow, brittle resin, nearly insoluble in water, light petroleom, and benzene, but easily soluble in alcohol, ether, and chloroform; when heated, it gradually softens, and is liquid at 90°. It has neither basic nor acid properties, and can be boiled with a mixture of lead oxide and water without any appreciable decomposition. It is gradually decomposed by boiling with aqueous potash and soda, and loses its vesicating power, several acids being formed, some of which are members of the acetic series. When oxidised with nitric acid, a mixture of acids is obtained. Since it is not saponified by lead oxide and water, and as no glycerol could be detected among the products of its decomposition by alkalis, it is not a glyceride, and as it does not react with hydroxylamine or phenylhydrazine or sodium hydrogen sulphite, it is probably neither a ketone nor an aldehyde. The authors hold the view that the constitution is that of a lactone or anhydride of complicated structure.

E. C. R.

Poisonous Constituents of "Œnanthe crocata" and of "Cicuta virosa." By JULIUS POHL (*Chem. Centr.*, 1894, ii, 793—794; from *Arch. exp. Pathol. Pharm.*, 1894, **34**, 258—267).—The poisonous principle of *Œnanthe crocata* resides mainly in the rhizome. The chief symptom is shocks of clonic cramp, which finally cause general exhaustion and death from stoppage of respiration. *Œnanthotoxin*, $C_{17}H_{22}O_5$ or $C_{23}H_{42}O_{10}$, may be extracted from the root by alcohol; it is a dark brown, resinous substance with a peculiar odour. A few

milligrams exhibited to a frog produced cramp closely resembling that caused by picrotoxin, and in the course of half to one hour proved fatal.

Cicutoxin is similarly extracted from *Cicuta virosa;* it is somewhat richer in carbon than œnanthotoxin is, from which it also differs in the greater ease with which it dissolves in alkali, and the difficulty which attends attempts to solidify it by desiccation.

Whether these two substances are really different compounds or differ merely from the presence of impurities remains undecided.

A. G. B.

Opening of the Thiophen Ring by Piperidine. By ALBERT TÖHL (*Ber.*, 1895, **28**, 2217—2220).—In attempting to prepare amidothiophen by the action of secondary bases on haloïd derivatives of thiophen, it was found that whilst the influence of a very high temperature is necessary in the case of diethylamine and bromothiophen, the latter is decomposed by piperidine at 240°, yielding a basic product which does not contain sulphur. This *base*, which probably has the constitution $C_5NH_{10}\cdot CH{:}C{:}C{:}CH\cdot C_5NH_{10}$, is prepared by heating iodothiophen (12 grams) with piperidine (10·5 grams) for six hours at 200° in a sealed tube; it is a viscous oil, which gradually becomes darker and less mobile on exposure to air. When reduced by adding sodium to the solution in absolute alcohol, it yields *tetramethylenedipiperidide*, $C_5NH_{10}\cdot[CH_2]_4\cdot C_5NH_{10}$, a colourless oil which has the odour of coniïne, and boils at 290—300° (uncorr.); the *platinochloride* melts and decomposes at 220°.

Trimethylenedipiperidide, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$, is prepared by adding small quantities of trimethylenic bromide to a boiling solution of piperidine in benzene; it boils at 274—275° (uncorr.), and closely resembles the tetramethylene derivative. The *platinochloride* melts and decomposes above 240°, the *hydrochloride* is hygroscopic, and the *aurochloride* melts at 188—190°.

M. O. F.

Disubstituted Amidacetones. By RICH. STOERMER and O. DZIMSKI (*Ber.*, 1895, **28**, 2220—2227; compare this vol., i, 479).—When piperidylacetone (*loc. cit.*) is reduced, piperidine and isopropylic alcohol are formed.

Piperidylhydroxyisobutyric acid, $\begin{matrix} C_5NH_{10}\cdot CH_2 \\ | \\ O\text{———}CO \end{matrix}\!>\!CMe\cdot OH$, is obtained by adding anhydrous hydrogen cyanide to well-cooled piperidylacetone, and allowing the mixture to remain for 24 hours at the ordinary temperature; hydrolysis is effected by gently heating the liquid with concentrated hydrochloric acid, and it is then filtered, boiled with caustic potash, neutralised, evaporated, and the residue extracted with absolute alcohol. The substance forms white, lustrous crystals, and melts at 234°; it dissolves readily in water, but only sparingly in cold alcohol, and is insoluble in ether and chloroform. The *copper* derivative, $C_9H_{16}NO_3\cdot CuOH$, is hygroscopic, dissolving in water and alcohol with great readiness, but it is insoluble in ether and benzene; the solution is deep blue, and becomes colourless when heated with a few drops of hydrochloric acid. The alkali derivatives were obtained in the syrupy condition, and attempts to prepare alkylic

salts were unsuccessful. The *amide*, $C_5NH_{10}\cdot CH_2\cdot CMe(OH)\cdot CONH_2$, is formed in preparing the acid when the hydrolysis, by means of hydrochloric acid, proceeds very slowly; it crystallises from hot water in long, white needles, and melts at 153°. The *platinochloride* of the amide forms large crystals, and melts at 198°; the *aurochloride* is crystalline, and melts at 145°.

Dimethylamidoacetone, $NMe_2\cdot CH_2\cdot COMe$, is prepared by adding chloracetone to an aqueous, 30 per cent. solution of dimethylamine; it is a colourless oil, miscible in every proportion with water, alcohol, and ether, and becoming brown on exposure to air. It boils at 123°. The *hydrochloride* is crystalline and very hygroscopic, and the *platinochloride*, which forms beautiful crystals, melts and decomposes at 176°; the *aurochloride* and *methiodide* melt at 145—146° and 168° respectively. The *oxime* crystallises from benzene in needles, and melts at 99°; when the vapour is passed through a glowing tube an oily base is produced, probably a derivative of dihydroglyoxaline. The *phenylhydrazone* is an oil.

Diethylamidoacetone, $NEt_2\cdot CH_2\cdot COMe$, is a colourless oil which boils at 64° under a pressure of 16 mm., and at 155—156° under atmospheric pressure; it rapidly becomes brown on exposure to air, and is miscible with water, alcohol, and ether. The *hydrochloride* is less hygroscopic than the salt of the foregoing derivative; the *platinochloride* is crystalline, and melts at 176°; whilst the *aurochloride* is an oil, and the *methiodide* is hygroscopic. The *oxime* crystallises in flat prisms, melts at 49°, and forms a crystalline *platinochloride*; the *phenylhydrazone* is an oil.

Dimethylamidohydroxyisobutyric and diethylamidohydroxyisobutyric acids have been obtained as syrups, the aqueous solutions dissolving copper carbonate with development of a deep blue colour.

M. O. F.

***n*-Phosphines and *n*-Phosphonium Derivatives.** By C. A. August Michaelis and K. Luxembourg (*Ber.*, 1895, **28**, 2205—2211; compare this vol., i, 430).—*Tripiperidine*-n-*phosphine*, $(C_5H_{10}N)_3P$, is prepared by the action of piperidine (20 grams) on phosphorus trichloride (5·4 grams) in anhydrous ethereal solution at 0°; it is colourless, crystalline, melts at 37—38°, is slowly decomposed by water or alcohol, and more rapidly by acids; if the acid is highly diluted and the solution cooled, a portion of the base is reprecipitated by alkali, but most of it is resolved into piperidine and phosphorus acid, thus proving that the nitrogen is directly linked to phosphorus.

Tripiperidinemethyl-n-*phosphonium hydroxide*, $(C_5H_{10}N)_3PMe\cdot OH$, prepared from the iodide, is crystalline, strongly alkaline, and absorbs carbonic anhydride from the air. The *chloride* and *bromide* are colourless and readily soluble. The *platinochloride* is at first white, but is deposited from alcohol in large, red crystals melting at 175°. The *iodide* crystallises in thick, colourless, cubical crystals melting at 251—255°. The mother liquor deposits a second crystalline compound which is richer in iodine, and is probably $(C_5H_{10}N)_3P,3MeI$. Attempts to prepare methylphosphinic acid from the iodide or hydroxide were unsuccessful.

Tripiperidineethyl-n-*phosphinium iodide* resembles the methyl com-

pound, and melts at 178—179°. The *isobutyl* and the *benzyl* compounds are crystalline; the former melts at 172°, the latter is hygroscopic. The *sulphide*, $(C_5H_{10}N)_3PS$, is prepared by heating the phosphine and sulphur alone, or in presence of benzene; it crystallises from alcohol in colourless, lustrous plates, melts at 120°, dissolves in concentrated hydrochloric acid, is reprecipitated on dilution, and is also formed by the interaction of piperidine and phosphorus thiochloride. J. B. T.

Stereoisomeric Copellidines. By Ludwig Levy and Richard Wolffenstein (*Ber.*, 1895, **28**, 2270—2273; compare Dürkopf, *Annalen*, **247**, 90).—The authors have prepared copellidine by the reduction of aldehydecollidine by Ladenburg's method, and find that a considerable quantity of an *isocopellidine* is formed at the same time. The new base yields a crystalline *hydrochloride* which is very deliquescent, and which is much more readily soluble in acetone than the copellidine hydrochloride. The *hydrobromide* melts at 108—114° and the *aurochloride* at 75—85°. The base itself boils at 160—165°.

Both copellidines may be separated into their optically active isomerides by crystallisation of the tartrates.

The lævo-copellidine tartrate is more soluble than the dextro-compound, whereas the dextro-isocopellidine tartrate is more soluble than the lævo-salt. J. J. S.

Action of Hydrogen Peroxide on Copellidine. By Ludwig Levy (*Ber.*, 1895, **28**, 2273—2274).—When an acetone solution of copellidine is allowed to stand with a 10 per cent. solution of hydrogen peroxide for about 10 days, it is converted into *δ-amido-ε-methyl-α-ethylvaleraldehyde*, $COH{\cdot}CHEt{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}NH_2$, which distils under a pressure of 10 mm. at 111—113°, has a specific gravity of 0·9367 at 21°, and possesses characteristic reducing properties.

When warmed with zinc and hydrochloric acid, it yields copellidine, and when treated with sodium hydrogen sulphite solution gives *copellidinesulphonic acid* which melts at 139°. J. J. S.

Isoquinoline Derivatives. By Adolph Claus and Carl Gutzeit (*J. pr. Chem.*, 1895, [2], **52**, 9—22).—*Hydroxyisoquinoline*, $C_9NH_6{\cdot}OH$ [OH = 1 or 4], is best prepared from the corresponding amido-compound by heating it with fuming hydrochloric acid at 275—280° for six hours; it forms yellowish crystals melting at 130°, and is identical with the substance obtained by fusing the less soluble isoquinolinesulphonic acid (following abstract) with caustic potash. The *hydrochloride*, *platinochloride*, with $2H_2O$, and *sulphate* melt, or decompose, at 207°, 300°, and 279—280° respectively; the additive compounds with *methylic iodide*, *ethylic bromide* and *iodide*, and *benzylic chloride*, the three last containing each $2H_2O$, melt at 239°, 78° (200°), 80° (275°), and 117° (202°) respectively, the numbers in brackets referring to the anhydrous substances; by adding silver chloride, sulphate, and nitrate to the methiodide compound there were obtained a corresponding *chloride*, with $1\frac{1}{2}H_2O$, *sulphate*, and *nitrate* melting, or decomposing, when anhydrous, at 259°, 270—280°, and 172° respectively; with potassium dichromate, any of the methylic compounds

yield a brown *dichromate;* all the other compounds crystallise in yellow needles. By treating the methiodide, ethiodide, and benzylochloride with moist silver oxide, the corresponding quaternary ammonium hydroxide compounds are obtained; these crystallise with 1, 2, and $2H_2O$ respectively, are respectively yellow, yellow, and red in colour, and decompose at 130°, 160°, and 110°.

By boiling the hydroxyisoquinoline with ethylic iodide and alcoholic potash, *ethoxyisoquinoline* is obtained; this, in the impure state, formed a thick, brown oil; its *ethiodide* melts at 170°, and when heated with silver chloride, yields the corresponding *chloride*, which melts at 63°. *Amidoisoquinoline* yields a *methiodide* which melts at 228°; the *chloride* melts at 288°, the *nitrate* at 203°, and the sulphate at 230°. The *ethobromide* melts at 257°, the *ethiodide* at 216°, and the *benzylochloride*, with $2H_2O$, at 88° (218°). These all crystallise in yellow needles. When the methiodide, either of hydroxy- or amido-isoquinoline is treated with silver oxide, a quaternary ammonium hydroxide, insoluble in ether, is formed; if, however, caustic potash be used, instead of silver oxide, a substance is obtained which is soluble in ether, but which must yet be a quaternary base, since it yields the same hydrochloride as does the base obtained with silver oxide. This behaviour is characteristic of the derivatives of quinoline, not of those of isoquinoline. C. F. B.

Isoquinolinesulphonic acids. By ADOLPH CLAUS and ALEX. SEELEMANN (*J. pr. Chem.*, 1895, [2], **52**, 1—8).—When isoquinoline is heated with fuming sulphuric acid containing 50—60 per cent. of anhydride, two sulphonic acids are formed; at 115° the less soluble acid is formed in larger amount, at 250—260° the more soluble one. *Isoquinolinesulphonic acid*, $C_9NH_6{\cdot}SO_3H + H_2O$ [$SO_3H = 1$ or 4, formerly wrongly regarded as 3 or 2], is the less soluble acid; it crystallises in yellowish-green, monoclinic prisms [$a : b : c = 0{\cdot}6560 : 1 : 0{\cdot}4931$; $\beta = 83°\ 29'$] the *potassium salt*, with H_2O, crystallises in yellow rhombic prisms [$a : b : c = 0{\cdot}3063 : 1 : 0{\cdot}385$]; the *sodium*, *ammonium*, *calcium*, and *barium* salts form colourless crystals containing respectively $3H_2O$ $1H_2O$, $2H_2O$, and $9H_2O$. The more soluble *acid* [SO_3H probably = 3 or 2] was obtained, with H_2O, as a crystalline powder; its *barium salt*, with $6H_2O$, as a greyish-brown, granular mass. C. F. B.

Nitromethylisoxazolone. By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 2093—2101).—The product formed by the action of concentrated nitric acid on oximidomethylisoxazolone has most probably the constitution $CMe\begin{matrix}N\text{———}O\\ \vert\\ CH(NO_2){\cdot}CO\end{matrix}$, and is, therefore, *nitromethylisoxazolone*. The *sodium salt* is probably derived from the hydrated acid, and has the composition $C_4H_5NaN_2O_5 + H_2O$. Nitromethylisoxazolone is completely decomposed by boiling with alkalis, carbonic anhydride, nitrous acid, acetic acid, and hydrogen cyanide being among the products of the reaction. *Nitromethylethylisoxazolone*, $CMe\begin{matrix}N\text{———}O\\ \vert\\ CEt(NO_2){\cdot}CO\end{matrix}$, obtained by the action of ethylic iodide on the

silver salt, crystallises in long, silky needles, and melts at 68°. It is hydrolysed in the normal way by alkalis. The *phenylhydrazine salt* of nitromethylisoxazolone crystallises in yellow needles, and the *aniline salt* is also crystalline. Nitromethylisoxazolone is converted by concentrated aqueous alkalis in the cold into a substance which has the composition of *nitracetoxime*, $NOH{:}CMe{\cdot}CH_2{\cdot}NO_2$. It is a yellow oil, and yields hydroxylamine when treated with hydrochloric acid. Bromine converts nitromethylisoxazolone, in aqueous solution, into a *dibromo-derivative*, $C_3H_4Br_2N_2O_3$, which is also formed by the action of bromine on a chloroform solution of nitracetoxime. It crystallises in needles, and melts at 86°. When exposed to the air, it loses hydrogen bromide, and is converted into a *monobromo-derivative*, $C_3H_3BrN_2O_3$, which melts at 62°. A. H.

Aliphatic Amidoketones. By HERMANN KÜNNE (*Ber.*, 1895, **28**, 2036—2044; compare Abstr., 1893, i, 734).—*Methyl amidoethyl ketone hydrochloride*, $COMe{\cdot}CHMe{\cdot}NH_2,HCl$, is obtained by reducing methyl isonitrosoethyl ketone with stannous chloride and hydrochloric acid; it crystallises in slender, white needles, and melts at 111°, previously becoming brown. The salt is hygroscopic, and is readily soluble in alcohol; it reduces Fehling's solution. The *platinochloride* melts at 191—192°. The base combines with phenylhydrazine, forming dimethylphenylglyoxalosazone, which is identical with the diacetylosazone described by v. Pechmann. When the hydrochloride is heated on the water bath with potassium thiocyanate, *dimethylimidazolyl mercaptan*, $\begin{matrix}CMe{\cdot}NH\\ \|\\ CMe{-}N\end{matrix}\!\!>\!C{\cdot}SH$, is formed; it crystallises from boiling water in pale yellow needles, and blackens at 270°. The base has a bitter taste, and in aqueous solution develops a dark red coloration with platinum tetrachloride, and with gold chloride a blood red coloration. Oxidation with ethylic nitrite converts it into *dimethylimidazole*, $\begin{matrix}CMe{\cdot}NH\\ \|\\ CMe{-}N\end{matrix}\!\!>\!CH$, which crystallises from ether in yellowish, quadratic plates, and melts at 117°; the *aurochloride* crystallises in yellow prisms, and melts at 174°, and the *nitrate* crystallises from alcohol in pale yellow needles, and melts and evolves gas at 164°. *Dimethylimidazolone*, $\begin{matrix}CMe{\cdot}NH\\ \|\\ CMe{\cdot}NH\end{matrix}\!\!>\!CO$, is formed when the hydrochloride of methyl amidoethyl ketone is heated with potassium cyanate on the water bath; it becomes brown at 210°, and begins to sublime at 280°. Tetramethylpyrazine is obtained from methyl amidoethyl ketone by successive treatment with potash and mercuric chloride; on distilling off one half of the liquid, and neutralising the distillate, mercuric chloride solution precipitates the mercurochloride of tetramethylpyrazine.

Methyl amidobutyl ketone hydrochloride, $COMe{\cdot}CHPr{\cdot}NH_2,HCl$, is obtained by reducing isonitrosobutyl methyl ketone with stannous chloride and hydrochloric acid; it crystallises in slender, white needles, and melts at 169—170°. It reduces Fehling's solution when

heated. The *platinochloride* crystallises in orange-yellow, quadratic plates, and melts at 163°; the *sodium picrate*,

$$C_6H_{13}NO,C_6H_3N_3O_7,C_6H_2N_3O_7Na + H_2O,$$

becomes anhydrous at 100°, and melts at 118—119°. *Methylpropylimidazolyl mercaptan*, $\begin{matrix}CMe\cdot NH\\ \|\\ CPr-N\end{matrix}\!\!>C\cdot SH$, or $\begin{matrix}CPr\cdot NH\\ \|\\ CMe-N\end{matrix}\!\!>C\cdot SH$, is obtained by the action of potassium thiocyanate on methyl amidobutyl ketone; it crystallises from dilute alcohol in white needles, and melts at 254—255°. The solution in hydrochloric acid develops a deep red coloration with gold and platinic chlorides. On oxidation, it yields methylpropylimidazole, which was not isolated in the pure state; the *aurochloride* crystallises from water in golden-yellow prisms, sinters at 137°, and melts at 138—139°, and the *picrate* melts at 151°. *Methyl benzenesulphamidobutyl ketone* is obtained by the action of benzenesulphochloride on methyl amidobutyl ketone; it melts at 97·8°. *Methylpropylimidazolone*, $\begin{matrix}CPr\cdot NH\\ \|\\ CMe\cdot NH\end{matrix}\!\!>CO$, is prepared by heating methyl amidobutyl ketone and potassium cyanate on the water bath; it becomes brown at 235°, and melts and decomposes at 263°. Dimethyldipropylpyrazine is obtained by the successive action of potash and mercuric chloride on methyl amidobutyl ketone; the *aurochloride* melts at 110° and the *picrate* at 95°, sintering at 92—93°.

M. O. F.

Constitution of *n*-Phenylpyrazolone. By Ludwig Claisen (*J. pr. Chem.*, 1895, [2], **52**, 78—80).—A reply to v. Rothenburg (this vol., i, 570). C. F. B.

Syntheses in the Pyrazole Series. By R. v. Rothenburg (*J. pr. Chem.*, 1895, [2], **52**, 23—44 and 45—48).—*3-Phenylpyrazolone*, $C_9H_8N_2O$, is obtained by the condensation of hydrazine hydrate with ethylic benzoylacetate in alcoholic solution; it melts at 236°; its *sodium*, *calcium*, and *silver* salts were prepared, and its *hydrochloride*, which melts at 196°. When it is heated with benzaldehyde, 2 atoms of hydrogen are replaced by the group CHPh, and *4-benzylidene-3-phenylpyrazolone*, $\begin{matrix}N:CPh\\ |\\ NH\cdot CO\end{matrix}\!\!>C:CHPh$, is formed; this is a red, crystalline substance melting above 250°. When 3-phenylpyrazolone is suspended in water and treated with aqueous nitrous anhydride, a yellow or red *isonitroso-derivative*, $C_9H_7N_3O_2$, melting at 188° or 184°, is formed; the red *silver salt* of this decomposes at 242°. From this salt, *ethyl*, *acetyl*, and *benzoyl* derivatives may be prepared by replacement of the silver atom; they are respectively red, yellow, and purple, and melt at 153°, 82°, and 142°. Alkaline reducing agents convert the isonitroso-compound back again into 3-phenylpyrazolone; acid reducing agents, such as zinc dust and acetic acid, reduce it to *4-amido-3-phenylpyrazolone*; this was not isolated, but its yellow *benzylideneamido-derivative*, melting at 152°, was prepared by the action of benzaldehyde, and it was oxidised by ferric chloride to a purple *3-phenylpyrazolonerubazonic acid*, $C_{18}H_{13}N_5O_2$, decomposing at 124°. The action

of the calculated quantity of acetic anhydride on 3-phenylpyrazolone in acetic acid solution converts it into a 1-*acetyl derivative*, which melts at 122° and yields a *silver salt*. Excess of acetic anhydride brings about the formation of a diacetyl compound, which must, however, be a derivative of isopyrazolone, 1 : 2-*diacetyl*-3-*phenylisopyrazolone*, $\begin{matrix}NAc{\cdot}CPh\\ |\\ NAc-CO\end{matrix}\!\!>\!CO$; this melts at 86°, and forms no salts. 3-Phenylpyrazolone also yields a yellow *dibromo-derivative*, melting at 189°, and a purple 4-*azobenzene derivative*, which melts at 207·5° and yields a yellow 1-*acetyl derivative*, melting at 199°, and a 1 : 2-*benzylidene* derivative, melting at 131°. 3-Phenylpyrazolone, when heated with methylic iodide and methylic alcohol, forms a 1-*methyl* derivative melting at 207°; when treated in alkaline methyl alcoholic solution with methylic iodide, it yields a small quantity of a 4-*methyl derivative*, melting at 138°. 3-Phenylpyrazolone cannot be reduced in any simple manner; excess of permanganate oxidises it to benzoic acid, but it is converted by the amount of permanganate theoretically necessary to oxidise it to benzoylformic acid into yellowish *phenylimidoacetic acid*, NH:CPh·COOH, which melts at 59°, and, when treated with phenylhydrazine acetate, yields the yellow *phenylhydrazone* of *benzoylformic acid*, $N_2HPh{\cdot}CPh{\cdot}COOH$, melting at 152°. Acid oxidising agents, such as boiling solution of ferric chloride, convert 3-phenylpyrazolone into 3-*phenylpyrazolone blue*; the two CH_2 groups in two molecules being converted into the group C=C, and the two molecules thus joined together.

3-*Methylpyrazolone* yields a yellow 4-*dibromo*- and a purple 4-*azobenzene* derivative; these melt respectively at 182° and 197°. With methylic iodide and methylic alcohol, it yields 1 : 2 : 3-*trimethylisopyrazolone*; and, when treated with just enough permanganate to oxidise the methyl group to carboxyl, it is oxidised to pyruvic acid, together with a little pyrazolone-3-carboxylic acid.

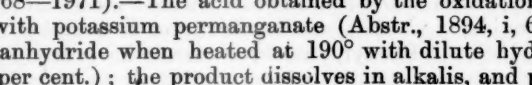
3 : 4-*Dimethylpyrazolone* is obtained by the action of hydrazine on ethylic methylacetoacetate, and melts at 249°. It yields a reddish-grey 4-*benzylidene derivative*, the CHPh group replacing the two 4-hydrogen atoms in 2 mols. of the pyrazolone; also a 1 : 2-*diacetyl* (iso), a 4-*nitroso* (?), and a 4-*azobenzene derivative*; these melt at 129°, 44°, 214°, and 188° respectively. It is oxidised by the amount of permanganate necessary to convert the two methyl groups into carboxyl to a base melting at 225°, the constitution of which was not ascertained.

3 : 4 : 4-*Trimethylpyrazolone* is obtained by the action of hydrazine on ethylic dimethylacetoacetate, and melts at 269°. It yields but few derivatives, both hydrogen atoms of the pyrazolone CH_2 group being now replaced by methyl. It does, however, yield a 1-*acetyl derivative*, which melts at 168°, and it is oxidised by the amount of permanganate just necessary to convert the three methyl groups into carboxyl, to the same substance as was obtained in the oxidation of dimethylpyrazolone.

Many of the experiments in the second paper have already been described (Abstr., 1894, i, 273, 344, 348, 384).—3-*Phenylpyrazole* is obtained, together with much of the 5-isomeride, by the action of

hydrazine on benzoylaldehyde in alcoholic solution; it melts at 228°. 3 : 4 : 5-*Trimethylpyrazole* is obtained by the action of hydrazine on methylacetylacetone; it melts at 138—139° and boils at 234—236°, and it is oxidised by alkaline permanganate to *pyrazole*-3 : 4 : 5-*tricarboxylic acid*, which crystallises with $2H_2O$, yields a crystallised *potassium dihydrogen salt*, and is converted into pyrazole when heated above 230°. 5-*Methylpyrazoline* was obtained by the action of hydrazine on crotonaldehyde in alcoholic solution; it is an oil boiling, with partial decomposition, at about 160°. The rest of the paper is devoted to theoretical considerations. C. F. B.

Oxidation of Tolualloxazine. By Otto Kühling (*Ber.*, 1895, **28**, 1968—1971).—The acid obtained by the oxidation of tolualloxazine with potassium permanganate (Abstr., 1894, i, 624) loses carbonic anhydride when heated at 190° with dilute hydrochloric acid (6—7 per cent.); the product dissolves in alkalis, and probably has a betaïne structure (I),



I. Alloxazine.

for it does not yield an acetic derivative, and evolves only traces of ammonia when boiled with strong aqueous alkalis. It melts at 284° with evolution of gas; at 250° it loses water, and the substance formed sublimes at 320°, yielding a yellow sublimate which is *alloxazine* itself. This substance melts above 310°; it has acid properties, and it is very stable towards acids and alkalis; when fused with caustic alkalis, it yields ammonia and hydrogen cyanide together with other products. C. F. B.

Apoquinine and its Rotatory Power. By Eduard Lippmann (*Ber.*, 1895, **28**, 1971—1972).—The author traverses Hesse's statements (*Ber.*, 1895, **28**, 1301). To get pure apoquinine, it is necessary to use dilute hydriodic, in place of hydrochloric, acid, and to precipitate the iodine with silver nitrate; ether then extracts a base which crystallises in colourless prisms containing ether of crystallisation, which is lost only slowly at 110°; the crystals have then become yellow, and have specific rotation $[\alpha]_D = -217{\cdot}1°$.

As to the formation of isomerides of quinine, this is probably one of the first stages of the reaction, but the whole subject is a difficult one. Two bases, melting respectively at 170—171° and 209—211°, have already been obtained. C. F. B.

Reduction of Cinchonine. By Fr. Konek v. Norwall (*Ber.*, 1895, **28**, 1843—1844).—The author maintains the accuracy of the results obtained by him in his work on cinchonine (this vol., i, 521), which has been criticised by Hesse (this vol., i, 630). A. H.

Cinchonicine. By Ferdinand Roques (*Compt. rend.*, 1895, **120**, 1170—1173).—Cinchonicine, obtained from the oxalate after the

latter has been carefully purified by repeated recrystallisation, will not crystallise from its ethereal solution in presence of air, but deposits more or less oily, amorphous products, as described by previous observers. If, however, the ethereal solution is dried by means of potassium hydroxide, and evaporated in a current of hydrogen at a comparatively low temperature, the alkaloïd separates in crystals. The best results are obtained by evaporating first at about 25° or 30°, and finally at the ordinary temperature.

Cinchonicine has the composition $C_{19}H_{22}N_2O$, and its crystals are long, amber-yellow prisms with curved faces, belonging to the triclinic system. It melts at 49—50°, alters rapidly when exposed to air, deliquescing to a syrupy liquid, and dissolves in the ordinary solvents, but crystallises only from ether. Its rotatory power in a 1 per cent. alcoholic solution is $[\alpha]_D = +48{\cdot}25°$, and in presence of 2 mols. HCl, $[\alpha]_D = +28{\cdot}72°$. The base liberates ammonia from ammonium chloride, and is readily precipitated by picric acid.

The double cinchonicine zinc chloride, $C_{19}H_{22}N_2O,2HCl,ZnCl_2 + 2H_2O$, and the analogous cadmium compound, crystallise in colourless, transparent needles; the methochloride in colourless, anhydrous needles, which melt at 159° (corr.), and the methiodide in yellow, anhydrous crystals, which alter somewhat readily; the ethobromide is similar to the methochloride, whilst the ethiodide forms a fine, yellow, anhydrous powder, which alters somewhat readily. The hydrochloride and hydrobromide have not yet been isolated.

The substance described as cinchonicine by W. v. Miller and Rohde (this vol., i, 434), does not seem to be identical with the cinchonicine isolated by the author. C. H. B.

Alkaloïds of Fumariaceæ and Papaveraceæ. By J. A. Battandier (*Compt. rend.*, 1895, **120**, 1276—1277).—The crude alkaloïds from Papaveraceæ, such as *Bocconia*, *Hypecoum*, *Eschscholtzia*, and *Glaucium*, give with sulphuric acid a reaction very similar to that of fumarine. The root of *Bocconia frutescens* contains fumarine identical with that obtained from *Fumaria*; another alkaloïd, which the author calls *bocconine*, and which gives a peach-blossom colour with sulphuric acid; traces of a third, which gives reactions similar to those of chelidonine; and a large quantity of chelerythrine.

Fumarine, some time after it has been precipitated, becomes only slightly soluble in water and most organic solvents, even at their boiling points, but is very soluble in chloroform. Its hydrochloride crystallises in heavy, transparent needles. With cold, concentrated sulphuric acid, fumarine gives a deep violet, almost blue, coloration, changing to brownish-black on the addition of potassium dichromate; traces of bocconine seem to modify this coloration.

Bocconine is relatively somewhat soluble in water and most neutral solvents, and crystallises in white, nacreous, silky tufts. The hydrochloride crystallises in similar forms. With most reagents, it gives reactions very similar to those of fumarine, but its salts are more soluble, and the colour with sulphuric acid is characteristic.

Chelerythrine is present in somewhat high proportions in the bark of *Bocconia*, to which it gives its red colour. When boiled with con-

centrated nitric acid, the deep red solutions of chelerythrine are decolorised, but on adding excess of ammonia, the liquid becomes red. *Eschscholtzia californica* grows readily in Algeria, and the juice of the root is rich in chelerythrine.

Glaucine.—The glaucine described by Probst contained small quantities of fumarine; when carefully purified it gives only a very faint, greenish-blue tint with concentrated sulphuric acid. On heating, however, the deep violet compound described by Probst is always obtained. The hydrobromide and hydriodide are the only glaucine salts that crystallise readily; the latter is less soluble in water than the former. C. H. B.

Yellow Colouring Matter of the Urine. By ARCHIBALD E. GARROD (*Proc. Roy. Soc.*, 1894, **55**, 394—407).—For previous work compare Thudichum (*Brit. Med. Journ.*, 1864, **2**, 509) and Schunck (*Proc. Roy. Soc.*, 1867, **16**, 85). Uroblin, hæmatoporphyrin, and, occasionally, uroerythrin occur as pigments in urine, but the quantity of each is too small to account for the yellow coloration. The author has succeeded by the following process in extracting a new colouring matter. The concentrated urine is saturated with pure ammonium sulphate, filtered, and to the filtrate absolute alcohol is added; this causes it to separate into two layers, the upper alcoholic layer containing the pigment. The latter, purified by a tedious process, the details of which are given in the paper, is ultimately obtained as a brown, amorphous mass. The substance thus obtained is not quite pure, but usually contains a little urea mixed with it. It is very hygroscopic, and readily soluble in water and in rectified spirit, but less so in absolute alcohol, and quite insoluble in ether, benzene, or chloroform. The solution shows no absorption bands, does not fluoresce when zinc chloride and ammonia are added, and is readily decolorised by nascent hydrogen. The solution, when treated with nitric acid, gave the xanthoproteic reaction. Precipitates containing the bulk of the pigment were obtained with lead acetate, mercuric acetate, silver nitrate, phosphotungstic acid, and phosphomolybdic acid, but not with mercurous acetate. When a colourless solution of uric acid is added to a solution of the pigment and allowed to crystallise, yellow or brown crystals are obtained which are indistinguishable from those of natural urinary sediments. The author thinks that the products obtained by Thudichum, Tichborne, and Schunck are probably the same as his, only in a more or less impure state. J. J. S.

Reduction of Alkaline Copper Solutions by Proteïds. By EDMUND DRECHSEL (*Zeit. physiol. Chem.*, 1895, **21**, 68—70).—Krukenberg stated that at the boiling temperature there is in the so-called biuret reaction of proteïds a reduction of the cupric to cuprous oxide, the latter, however, remaining in solution. The present research shows that this reduction also occurs at the ordinary temperature; it is, however, very slow and incomplete. The solutions were kept for a year before they were examined. The substances used were Witte's peptone, and deutero-albumose. This result does

not necessarily mean that these substances contain a carbohydrate radicle, for many substances not carbohydrates reduce Fehling's solution. W. D. H.

Mode of Combination of Sulphur in Albumin. By F. SUTER (*Zeit. physiol. Chem.*, 1895, **20**, 564—582).—The following substances were tested in order to ascertain to what extent the sulphur which they contain is precipitated when they are heated in alkaline solution with lead acetate. The precipitation from cystine, with or without peptone, and cysteïne is incomplete, and proceeds very slowly, only 60 per cent. being obtained after 9·5 hours. Hair and feathers deposit 98·8 and 98 per cent. after 9 and 15 hours respectively; egg albumin and peptone behave in a similar manner; these compounds therefore resemble cystine. The production of a clear filtrate is no criterion of complete precipitation. Under similar conditions the sulphur is completely precipitated from thiocarbamide and allylthiocarbamide. Attempts were made to isolate cystine or cysteïne from residues obtained during the preparation of tyrosine, but without success; these substances are not, therefore, direct decomposition products of horn, but they may posssbly be formed in traces. The above mother liquor contained α-thiopropionic acid in rather small quantity; this was recognised by its *benzyl* derivative which crystallises in colourless prisms, melts at 73°, and is identical with the synthetical compound obtained from benzylic mercaptan and ethylic α-bromopropionate. A second substance, which has strongly acidic properties, and contains sulphur, was also isolated from the tyrosine mother liquor; it gives a blue coloration with ferric chloride, and a fugitive violet with copper sulphate; it does not yield a benzyl derivative, and is possibly thioglycollic acid (compare following abstract), α-Thiopropionic acid is not a primary decomposition product of albumin. By the action of hydrogen sulphide on pyruvic acid in aqueous solution, in presence of sodium acetate, α-thiopropionic acid is formed; pyruvic acid is also not a primary decomposition product of albumin, as it is not present in the tyrosine mother liquor.

J. B. T.

Sulphur Derivatives of Albumins and their Interrelationship. By EUGEN BAUMANN (*Zeit. physiol. Chem.*, 1895, **20**, 583—585; compare preceding abstract).—The formation of α-thiopropionic acid from cysteïne resembles that of hydroxyparacoumaric acid from tyrosine. It is very probable that the ethylic sulphide, which J. J. Abel found in dog's urine, particularly after a meat diet, is produced by the decomposition of α-thiopropionic acid. Nencki has shown that methylic mercaptan is formed during the decomposition of albumin, and should Suter's observation of the occurrence of thioglycollic acid be confirmed, these would appear to be related, like ethylic mercaptan and α-thiopropionic acid. The primary thio-decomposition product of albumin is unknown; possibly it may prove to be a thioaspartic acid, $NH_2{\cdot}C(SH)(COOH){\cdot}CH_2{\cdot}COOH$. J. B. T.

The Behaviour of Caseïn in Ammoniacal Magnesium Chloride Solution. By WACLAW V. MORACZEWSKI (*Zeit. physiol.*

Chem., 1895, **21**, 71—78).—A solution of caseïn free from ash (caseïnogen), when mixed with ammoniacal magnesia mixture, proceeds, after some days, to deposit sphæroliths; these, by attention to details, described in full in the paper, can be obtained in the form of aggregations of needles. They contain 45 per cent. of ash, and 14·98 per cent. of nitrogen. The nature of this proteïd compound of magnesium is, however still uncertain.

Nucleïn also yields a crystalline deposit with ammoniacal magnesia mixture. W. D. H.

Precipitation of Toxalbumins by Nucleïc acid. By M. Tichomiroff (*Zeit. physiol. Chem.*, 1895, **21**, 90—96).—Ricin is precipitable by nucleïc acid. The precipitate can be redissolved, and, when tested on animals, is found to be still as poisonous as before. The same was found to be true for tetanus poison and diphtheria poison. The addition of nucleïc acid to solutions of cholera poison and to cultures of streptococci, *Staphylococcus aureus*, and typhoid bacilli (in all cases freed from the growth of micro-organisms) produced a precipitate, which, however, was not poisonous. From putrefying beef, the precipitate was also not active; but a poisonous precipitate was obtained from putrefying fish. W. D. H.

Amylase. By Jean Effront (*Compt. rend.*, 1895, **120**, 1281—1282).—An infusion of barley prepared at the ordinary temperature, boiled and filtered, greatly increases the diastatic power of malt, and thus resembles aluminum and vanadium salts, asparagine, picric acid, &c. (Abstr., 1893, i, 187). Since, however, in all cases the saccharifying power only is increased, whilst the liquefying power is practically unaffected, and the effect disappears in presence of such quantities of amylase as are required to produce energetic saccharification, the increase in saccharifying power is more apparent than real.

A comparison between the saccharifying and liquefying powers of malts yields better results than the methods of Kjeldahl and Lindner. The substance to be examined is extracted with eight times its weight of water. The saccharifying power is measured by the volume of the solution required to produce in an hour, at 45°, 0·25 to 3 grams of maltose per 100 c.c. of starch paste, the experiment being made with 150 c.c. of a 1 per cent. solution of starch. The liquefying power is expressed by the volume of the solution required to liquefy in 10 minutes, at 80°, 20 c.c. of milk of starch containing 40 parts of starch in 100. The ratio between the saccharifying and liquefying powers in good malt is 100 to 120, but in presence of substances that increase the saccharifying power it may rise to 200—400. The diastase of the crude barley shows a ratio of more than 1000. The saccharifying power being equal, the value of two malts is proportional to the ratios between the saccharifying and liquefying powers. C. H. B.

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